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AUTOMATIC CONTROL OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR

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AUTOMATIC CONTROL OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR

Summary

This report covers the work during the first two years on grant number WPD-175-01-67 and WPD 175-02-67 from the Federal Water Pollution Control Administration. The report is presented as four separate research papers on the several phases of the grant. All programs were conducted as proposed in the original grant application. A summary of each paper follows:

1. "A Study of the Reaction Kinetics of a Completely Mixed Activated Sludge Reactor"

The reaction kinetics of a completely mixed activated sludge reactor were measured at reactor pressures ranging from 0-100 psig. The reactor was fed primary effluent from the University of Connecticut treatment plant. Second order kinetics were shown to fit the data with accuracy equal to that from Monod kinetics. The synthesis coefficient, Y, was found to decrease as the reactor pressure was increased.

2. "The Effect of Changes in pH on the Performance of a Completely Mixed Activated Sludge Reactor"

A mathematical model was developed which described the effect of pH on the completely mixed activated sludge system. Experimental data obtained with bench-scale apparatus indicated that the model was of the correct form. The equilibrium constant for the adsorption of H^+ onto activated sludge in an acid environment had an experimentally determined value of 710 $(mg/l)^{-1}$ (pK = 2.85) which was independent of the suspended solids concentration.

3. "Determination of Mixing in a Gas Sparged Reactor"

The purpose of this project is to determine under what conditions complete mixing can be attained in a gas sparged reactor. The immediate application of gas sparged reactors is in the activated sludge waste water treatment process. The axial dispersion coefficient, D_L, which provides a measure of the degree of mixing flow was determined from a pulse tracer injection of a known concentration of NaCl

solution. The dispersion coefficient was correlated in terms of a Peclet Number, $\frac{U_L d_t}{D_L}$, based on liquid flow velocity and tube diameter. The Peclet Number was calculated from residence time distribution data involving the statistical variance from the solution to the differential diffusion model equation.

The reactor was found to be essentially completely mixed for superficial gas velocity greater than 0.03 ft/sec. For gas velocities greater than 0.03 ft/sec., the following generalized correlation was found:

$$Pe = \frac{U_L d_t}{D_L} = 2.80\,(Ug)^{-.118}(L/d_t)^{-.976}$$

4. "Response and Stability of a Completely Mixed Activated Sludge Reactor"

A mathematical model of a completely mixed activated sludge reactor was developed using Monod kinetics. The numerical solution of the resulting set of nonlinear differential equations was compared with the linearized analytical solution. The error between the nonlinear and linearized responses about an arbitrary steady state are shown for several step changes in inlet flow rate, carbon concentration, and sludge concentration. A stability analysis indicates that the reactor is stable over a wide range of operating conditions.

Significance of Results

Since the production of sludge in an activated sludge reactor was shown to decrease as the pressure increased, these results may be of benefit to those operations where sludge disposal is a problem. Since the concentration of dissolved oxygen in water at equilibrium with air at 100 psig is approximately the same as that of pure oxygen at atmospheric pressure, these kinetic results may aid current FWPCA research programs using pure oxygen [1], and liquid oxygen[2] in activated sludge reactors. These second order kinetics may also be of benefit to the Dallas demonstration plant in modelling their plant[3].

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[1] "Oxygen Bids for Sewage Treatment Role", Environmental Science and Technology, 3(2), 109 (February 1969)

[2] Loxination - New Sewage Treatment Process", Chemical and Engineering News, p. 50, April 28, 1969.

The buffering ability of activated sludge has been well known for some time. However, our model replaces some of the qualitative description with quantitative equations which appear to describe the effects. More testing of the model is necessary before it can be generally accepted.

Dzielenski's paper shows how to design a sparged reactor completely mixed. Since all models assume complete mixing, it is necessary that the reactor approach complete mixing as closely as possible.

Before controls are applied to a chemical reactor, the reactor is analyzed for its dynamic stability. As might be expected, the activated sludge reactor was shown to have very broad regions of stability. These results were presented at the AIChE meeting in New Orleans during March 1969.

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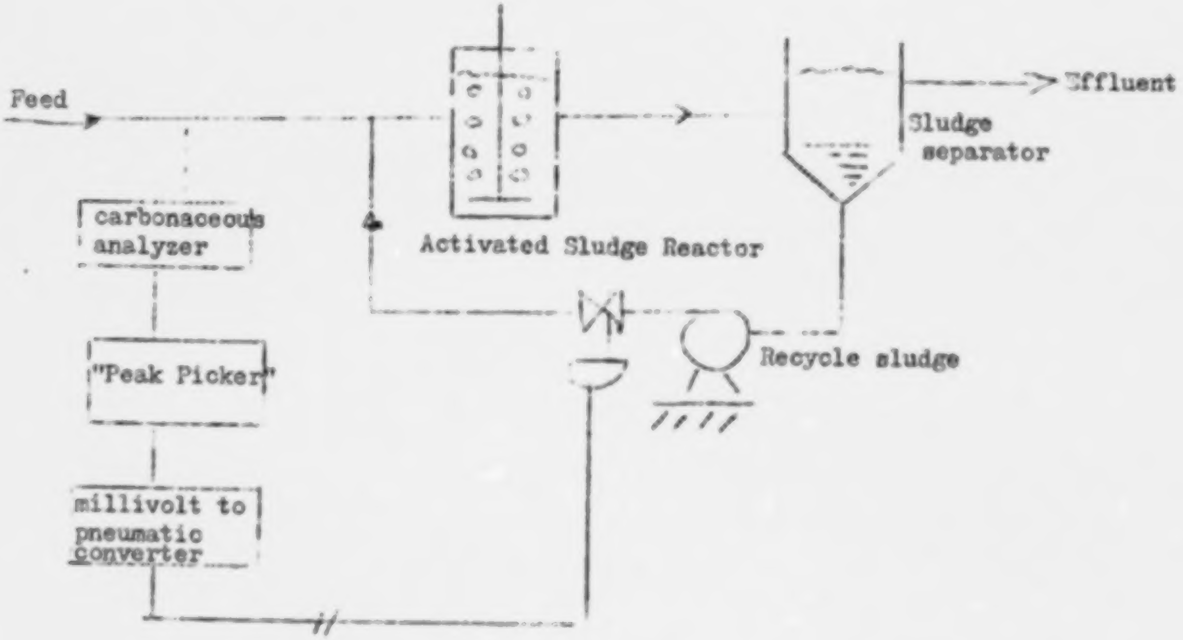
[3] Graeser, H.J., and Haney, P.D., "Dallas Builds Center to Study Wastewater Reclamation", Water and Wastes Engineering, 5 (12), 34 (December 1968).

Proposed Work for the Third Year

During the terminal year of this three year grant, we propose to apply these results on a feed forward control scheme around our pilot activated sludge reactor. The proposed control scheme is shown below:


Feed
carbonaceous analyzer
"Peak Picker"
millivolt to pneumatic converter
Activated Sludge Reactor
Effluent
Sludge separator
Recycle sludge

The level of carbon into the reactor will be sensed by the carbonacecus analyzer which will give a series of peaks, the height of which will be proportional to the carbon input level. The "peak picker" will give a steady output proportional to the peak heights, resembling a stair case function. The converter will change the electrical signal from the "peak picker" to a 3-15 psig air signal which can operate a pneumatic valve in the sludge recycle line. Hence, as the concentration of input carbon increases so will the amount of recycle activated sludge also increase giving a relatively stable carbon level in the reactor output.

Most of the equipment has been purchased during the first two years of the grant. During the third year we will operate the system and gather the data.

V

A STUDY OF THE REACTION KINETICS OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR

Leonard J. Kaplan
Herbert E. Klei

Department of Chemical Engineering
The University of Connecticut
Storrs, Connecticut

SUMMARY

The reaction kinetics of a completely mixed activated sludge reactor were measured at reactor pressures ranging from 0-100 psig. The reactor was fed primary effluent from the University of Connecticut treatment plant. Second order kinetics were shown to fit the data with accuracy equal to that from Monod kinetics. The synthesis coefficient, Y, was found to decrease as the reactor pressure was increased.

I. INTRODUCTION

Increasing water pollution problems in the world today have led to concentrated study in the area of sewage treatment and waste disposal. More efficient methods are needed to clean up polluted rivers and minimize the pollutants in sewage so as to avoid polluting more of our natural water sources.

At present, the most effective method of reducing the organic content of liquid waste is by aerobic biological oxidation. The organic content of biochemical oxygen demand (BOD) of sewage is converted to products which are not pollutants. This conversion is achieved by bringing into contact with the organic pollutants, in the presence of dissolved oxygen, micro-organisms which use them as food. These micro-organisms are referred to as biological sludge or mixed liquor suspended solids.

Much work has been done to determine the biochemical reaction which takes place during biological oxidation. Though not completely understood, it is known that two major reactions take place simultaneously. They are:

$$\text{Organic Wastes} + O_2 \xrightarrow{\text{micro-organisms}} CO_2 + H_2O + NH_3 + \text{Energy} \qquad (1)$$

$$\text{Organic Wastes} + O_2 \xrightarrow{\text{micro-organisms}} \text{New Cells} \qquad (2)$$

Equation 1 represents the complete oxidation from which the energy is obtained. This energy is used by the micro-organisms for bodily functions such as growth, locomotion, and reproduction. Equation 2 represents the synthesis of new cells. The conditions under which the oxidation takes place dictates which one of the reactions predominates. If limited amounts of food are present and there is an excess of dissolved oxygen, reaction 1 predominates. Having an abundance of food and a limited amount of dissolved oxygen pushes the overall reaction toward the synthesis of more cellular matter.

The two main processes for the treatment of sewage which depend on the biological oxidation reaction are trickling filters and activated sludge units.

Trickling filters are made up of large beds of packing medium such as gravel and coke which is supported by some sort of under-drain system. The sewage is allowed to trickle down through the bed where it comes in contact with biological sludge which grows on the packing. The needed oxygen for oxidation is supplied by the amounts dissolved in the sewage and through the air entering the bed by ventilation.

In the activated sludge process, all of the reactants for biological oxidation are brought together in a liquid solution. The process has definite advantages over trickling filters.[19] Increased efficiencies in BOD removals and smaller equipment sizes are among a few.

Sewage treatment using the activated sludge process began about 60 years ago. Since then, the process has undergone many changes in operation, design of equipment and mathematical models describing the system.[15,21,23] One of the most important improvements has been the type of reactor used for bringing the sludge, organic wastes, and oxygen into contact with each other.

Conventional systems use long trough which act like plug flow reactors. This type of system is in wide use today but has several disadvantages. In order for the micro-organisms to function most efficiently, the environment in which they live must remain at fairly constant conditions. In the conventional activated sludge system, the environment is constantly changing as the BOD content of the input to the sewage treatment plant changes. This makes the process difficult to control.

The newest approach is the completely mixed reactor operating continuously. McKinney[12] and other researchers have shown this design to be the most effective.[7,8,13,16] It is for this reason that this type of reactor was used for this study. Figure 1 shows a flow sheet for a typical completely mixed activated sludge system.

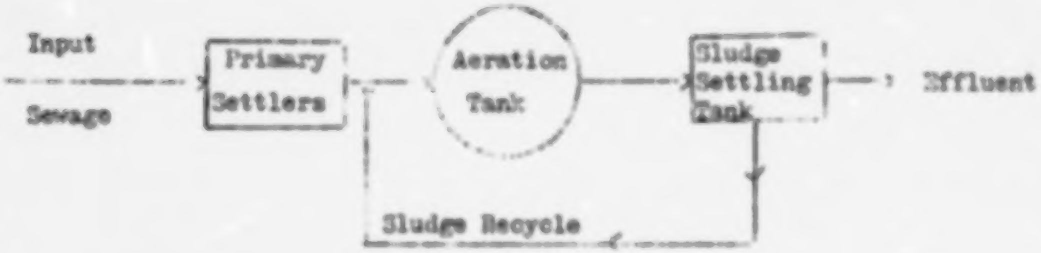


Figure 1

The raw sewage enters the aeration tank after having large suspended solids removed in primary clarifiers. The sewage is then completely mixed with the sewage all ready present in the aeration tank. Mixing is accomplished by either mechanical means or by air which is forced into the reactor through spargers. Using this method, the environment within the reactor is kept at almost constant levels. For instance, BOD concentrations greater than normal values are almost instantly diluted inside the reactor and the overall change is not sufficient to disturb the growth pattern of the activated sludge. Thus the sludge acts most efficiently since it does not have to keep adjusting to radically different conditions. The sludge which is settled out in the final settling tank is recycled back into the input stream to the aeration tank in order to maintain the correct concentration of activated sludge for the particular running conditions.

The micro-organisms which are present in the flocculant masses have been referred to as activated sludge for their unique ability to absorb collodial and suspended matter from solution. It acts in much the same way as activated carbon when used as a filtering device. This adsorption is responsible for an initial BOD removal as the feed enters the reactor.

The key to finding a mathematical model to accurately describe a completely mixed activated sludge reactor, so as to be able to control its operation, lies in formulating suitable kinetic expressions. These expressions would have to describe the removal of BOD by the activated sludge by both adsorption and biological oxidation. In the last 10 years much work has been done in this area and is discussed in detail in the next section of this report.

In order to begin to formulate kinetic expressions, the growth characteristics of the micro-organisms which comprise the activated sludge must be studied. Microbiologists have studied the life cycles of organisms such as bacteria, which are a major part of the make-up of activated sludge. The rate of growth of these micro-organisms is directly related to the rate of removal of BOD from solution. Figure 2 shows a typical growth curve for a bacteria culture introduced into a food source.

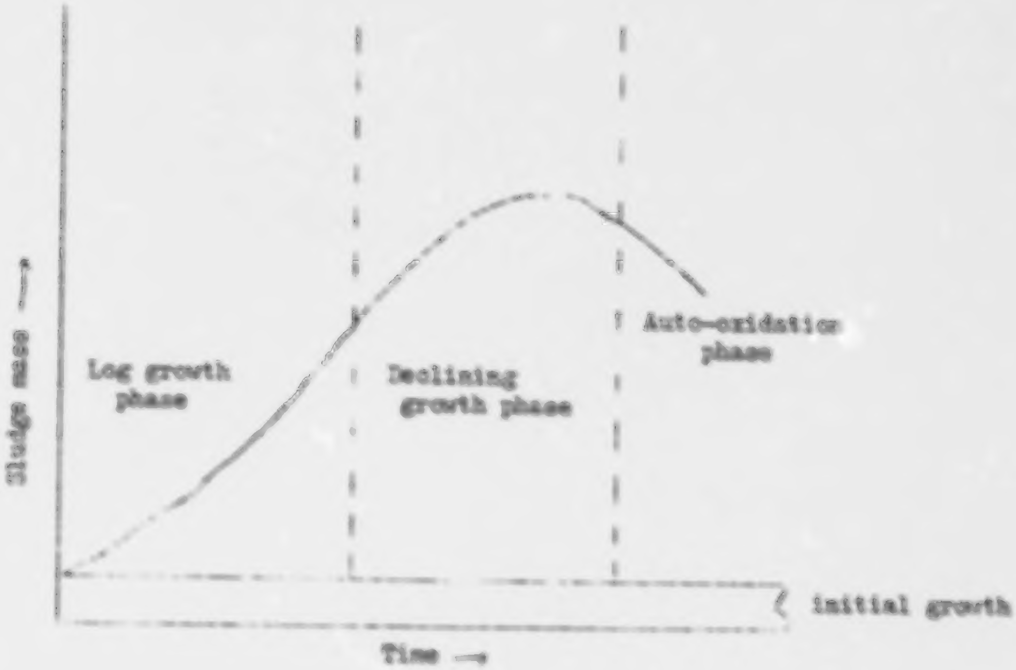


Figure 2

The three different periods represented are:

1) The Logarithmic Growth Phase - this period has an increasing rate of growth due to unlimited amounts of food.
2) Declining Growth Phase - decrease in food concentration begins to limit the growth rate of the bacteria.
3) Auto-oxidation Phase - due to the disappearance of food the bacteria begins to feed on itself. Oxidation of cellular matter exceeds the synthesis of new cells.

McCabe and Eckenfelder[11] have used the fact that BOD removal is directly related to the rate of sludge growth and drawn up expressions which describe the rate of removal of BOD for each of the three different phases of the growth curve (Figure 2). Consideration is made for the initial BOD removal due to adsorption.

Other kinetic expressions have been arrived at by different consideration. The Michaelis-Menten equation,[29] represented in equation 3, is derived from enzyme reaction kinetics and has been accepted by many researchers.[2,17,20,22]

$$v = Vs/Km + S \qquad (3)$$

where:

v = rate of production formation
S = concentration of substrate
Km = Michaelis-Menten constant
V = maximum rate of production (constant)

A similar equation was arrived at by Monod[18] from the growth stuies of bacteria cultures.

Because of the many proposed kinetic equations and the confusion as to which one correctly described what is happening inside an activated sludge reactor, this study tests proposed kinetic expressions to see which one works the best.

Once the best kinetic expression is determined, we are in a good position to determine the influences of temperature and pressure on the rate of BOD removal, sludge growth, and the overall operation of the activated sludge system. Temperature effects have been studied by Ludzack[10] and others, but almost no work has been done to determine pressure effects.

II. PREVIOUS WORK

The last twenty years have seen a considerable amount of research and study done to improve the operation of the activated sludge method of waste treatment. As mentioned previously, the acceptance of the completely-mixed concept has been the most important physical design advancement.

A.A. Kalinske[7] reported in 1950 that, using an aeration tank which he called the Aero-Acdelator, greater biological loadings could be handled. In a later paper[8] he referred to this type of reactor as being completely mixed.

Biological loadings of 4-6 times greater than the amount normally handled by conventional activated sludge aeration were reported. The micro-organisms were kept in a uniform state of growth and at the same time they were kept in the presence of oxygen.

McKinney[12,13,14] found that the completely-mixed system was the best as far as control considerations were concerned. By proper designing it was possible to take a waste of any organic strength and produce an effluent of a desired organic strength. He also substantiated the fact that the completely-mixed system produced a more uniform biological population which was capable of performing with much greater efficiency.

Most of the disagreement and misunderstanding in the activated sludge process comes from the kinetics involved in the removal of the organic concentration. Unfortunately this is the most important bit of information needed to be able to arrive at an accurate mathematical model, to describe the whole system.

Microbiologists had studied the rate of growth of bacterialogical cultures for use in the fermentation industries. This certainly was a good place to start since the same micro-organisms are present in activated sludge. Monod[18] formulated an expression which described the rate of growth of bacteria in a growth limiting substrate (equation 4).

$$\mu = \mu_{max} (S/K_s + S) \qquad (4)$$

where:

$\mu = 1/x \frac{dx}{dt}$ = the specific growth rate of bacteria cells
μ_{max} = maximum growth rate when the substrate is unlimited
S = concentration of the growth-limiting substrate
K_s = the substrate concentration at which the specific growth rate observed is 1/2 the maximum value
= saturation constant
x = mass of cells per unit volume

It follows the same form as the Michaelis-Menten equation (equation 3), except for differences in nomenclature. This form of kinetic expression has been used and accepted as workable by many researchers studying the activated sludge process.[2,17,20,22]

Another approach, already discussed, is the method used by McCabe and Eckenfelder[11]. Mathematical expressions are formulated which describe the behavior of the activated growth curve. Two first order equations are used, each one describing a different portion of the growth curve. Unfortunately, each of these equations show the BOD removal to be a function of either the BOD concentration or the activated sludge concentration. This may be true for just one part of the growth curve at a time, but in order to have one expression that describes the entire curve, the rate of BOD removal has to be a function of both BOD and sludge concentrations.

With the above in mind, Ville, Lynn, and Rivera[25], used a second order model and ran batch reactor tests to determine the reaction rate constant (Table 1).

Most of the research work done in testing kinetic models and determining rate constants has been done with artificial feeds with constant concentrations. Some of the studies were done using batch reactors while others used bench scale completely-mixed reactors. Schulze[22], using a feed at constant temperature and concentration, studied the Michaelis-Menten and the Teissier formulation, in a completely-mixed bench scale reactor. He predetermined his reaction rate constants in batch reactors.

Reynolds and Yang[20] developed material balance equations to describe the completely-mixed activated sludge reactor running at steady state conditions. They used a synthetic feed of constant concentration, primarily made up of glucose and peptone. From their laboratory runs they concluded that the Michaelis-Menten kinetic expression was satisfactory. They determined values for the kinetic constants and for Y, the yield coefficient. The yield coefficient was defined by Monod[33], to be the weight of organisms produced per the weight of food substrate used. These values plus the data obtained by the other researchers mentioned in this report, are tabulated in Table 1.

Table I

Researcher	H		T		Ref.	Comments
	Value	Units	Value	Units		
Schulze	1.09	hr^{-1}	95.4	mg BOD/l	22	Synthetic feed of glucose & urea, etc. Constant temperature and feed concentration
Reynolds & Yang	.8	hr^{-1}	345	mg BOD/l	20	Feed of glucose & peptone
Middlebrooks	.0143	hr^{-1}	71.3	mg BOD/l		Run at steady st.
	.0051	hr^{-1}	13.2	mg BOD/l	17	3 lab runs
	.0147	hr^{-1}	173	mg BOD/l		1 pilot plant run
	.0051	hr^{-1}	12.4	mg BOD/l		Lot of scatter in data
Benedeck & Horavath	3.73	day^{-1}	21.98	mg BOD/l	2	Feed concentration not constant Actual treatment plant for runs
Ville (second order model)	.00128	$[(mg/l)day]^{-1}$			25	
	.00124	"				
	.00128	"				

Benedek and Horvath[2], two Hungarian researchers, used a feed from an actual waste treatment plant. They also used the Michaelis-Menten kinetic expression in the formulation of the mathematical description of the completely-mixed system. Though they did obtain values for the various constants, their mathematical methods are questionable. They derived equations for their system with the assumption that it was operating at steady state conditions. But since their system was an actual treatment plant, the feed concentration was changing constantly and therefore the system was not operating at steady state conditions.

Two variables which also have been studied to find out their effects upon the activated sludge process are temperature and residence time or flowrate. Ludzack[10] did studies on the effects of temperature on the working characteristics of activated sludge on a synthetic feed. He studied the sludge at temperatures of 5 and 30 C. He found that the micro-organism population was different at different temperatures. BOD removal was 10% higher at 30 than at 5, while the solids accumulation per unit weight of BOD feed was greater at 5 than at 30C.

Hunter, Genetelli, and Gilwood[6] found no significant trends evident in effluent levels and removal efficiencies with changes in temperature. They did find that Ludzack's observations about the different micro-organisms in the sludge at different temperatures was correct. As the retention times increased at constant temperature, the amount of activated sludge decreased and the BOD removal efficiencies increased.

As far as the effects of pressure on the operation of the completely-mixed activated sludge process are concerned, no work of any value has been done. This is one of the objectives of this study.

III. EXPERIMENTAL WORK

A) Pilot Plant

The activated sludge system used to study the effects of pressure and temperature was made up of a reactor, instruments for monitoring the variables, and controllers to keep the reactor in continuous operation automatically.

The reactor was constructed from a 5'6" long piece of 18" schedule 10, 304 stainless steel pipe. The bottom of the reactor, from which the effluent line protruded, was made from an 18" diameter, 304 stainless steel cap. The top of the reactor was constructed from an 18" - 150# flange, on which was mounted a 5" - 150# schedule 40, 304 stainless steel flange for the mounting of a 5" sight glass.

Lying in a straight line down the side of the reactor are three 4" sight glasses, mounted on 4", 150# schedule 40, 304 stainless steel flanges. The first is mounted on a 9 1/2" lone piece of 4" diameter schedule 40 stainless steel pipe, which is welded at 30 degree angle with the reactor. The other two sight glasses lie 3'2 1/2" and 6', respectively, from the top of the 18" flange making up the top of the reactor.

The oxygen needed for the biological oxidation enters the reactor by means of a six leg spider sparger connected to the air line. The sparger is composed of 1/2" schedule 40, 316 stainless steel tubing, each leg being 7 1/2" long and containing about 50 1/16" holes. The air line enters the reactor 7 1/4" from the top of the reactor and is connected to the sparger by a piece of 7'3/4" long and 1/2" schedule 40, 316 stainless stell.

In order to have a knowledge of the conditions of the reactor at all times, instruments for measuring dissolved oxygen, temperature, pressure, pH, and flow rate, were major parts of the entire system.

The temperature at various points within the reactor was obtained by five Honeywell iron-constant thermo-couples, which were placed along the length of the

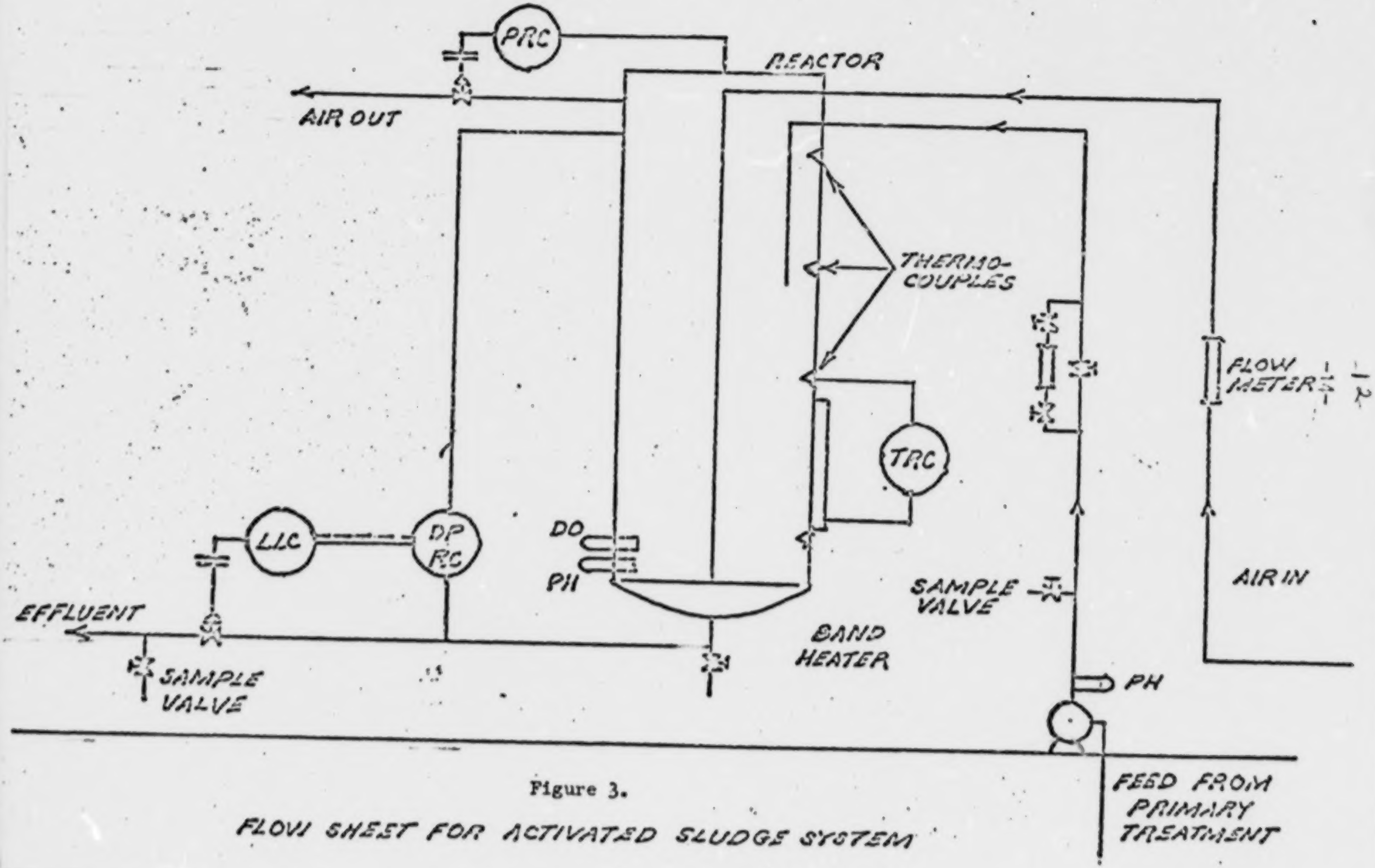
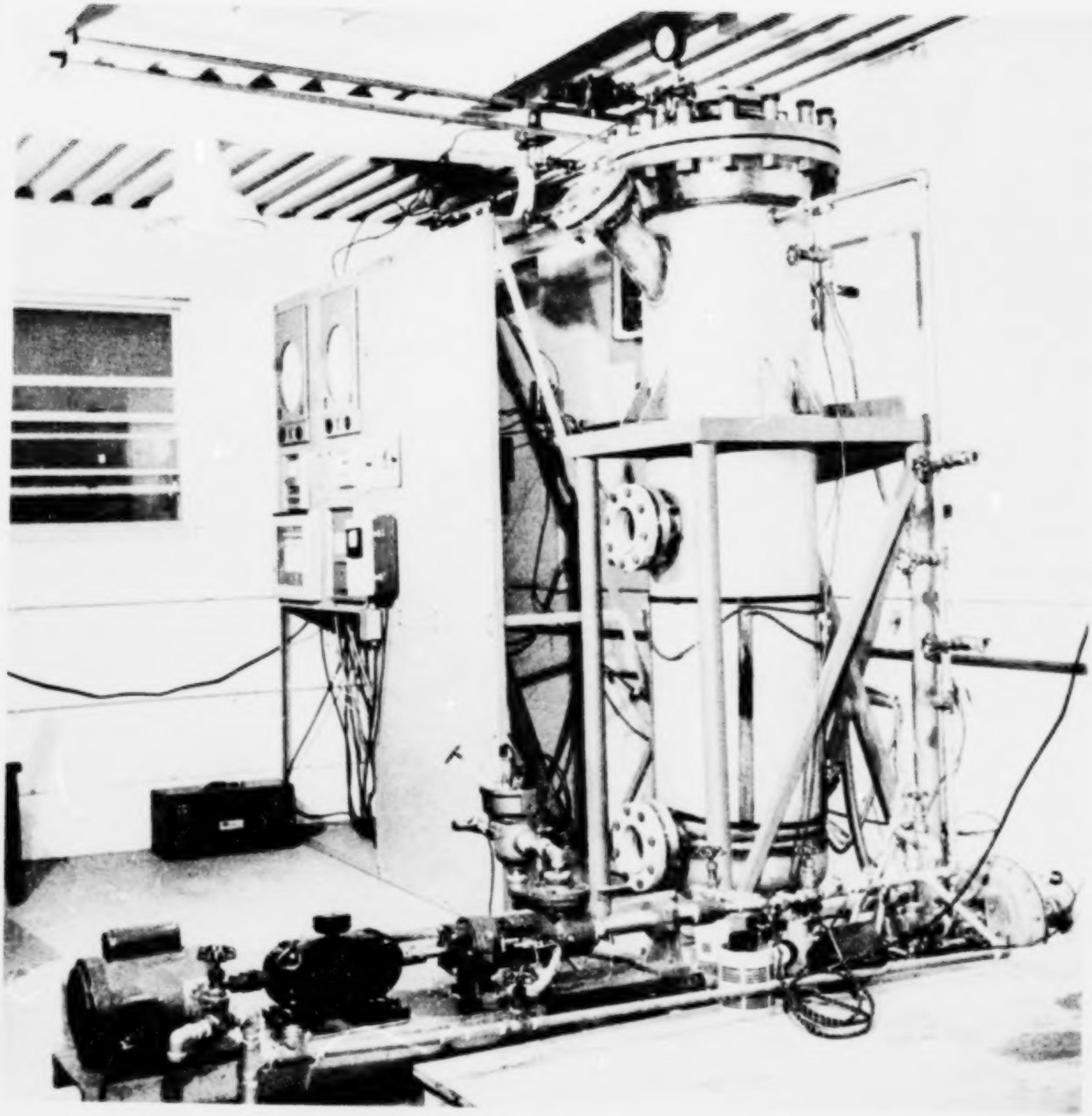

PRC
REACTOR
AIR OUT
THERMO-COUPLES
FLOW METER
TRC
LLC
DP RC
DO
PH
EFFLUENT
SAMPLE VALVE
SAMPLE VALVE
BAND HEATER
AIR IN
PH
FEED FROM PRIMARY TREATMENT

Figure 3.

FLOW SHEET FOR ACTIVATED SLUDGE SYSTEM



reactor. The first was mounted in the rear of the reactor, 10 1.2" from the top. The second was on the left side of the reactor, 1'9" from the top. The other three were mounted below the second, separated by a distance of 1'5 1/2". All five of the thermocouples were connected to an Esterline Angus Multipoint recorder, model E1124E. The lower thermocouple was connected to a Honeywell Controller, model R7161G. The controller, in turn, was connected to two Chromalox (Edwin L. Wiegand Co.) strip heaters. These heaters were strapped to the lower portion of the reactor. These heaters were approximately 1'9 1/2" long and were the sourse of heat to maintain the reactor at a fairly constant temperature. Two other strip heaters were connected to a Powerstat Variac (Superior Electric Co.), model 3PN116, to control the heat to the reactor manually if necessary. Average temperature readings were taken from a Weston Dial thermometer model 4300, which was mounted on the outside of the reactor, 3'11 1/2" from the top.

To measure the pH of the feed to the reactor, a Beckman Palladium Junction Reference and glass Silver-Silver Chloride electrodes were mounted on the lower rear of the reactor. Both sets were connected to a Beckman pH analyzer, model 900 giving us knowledge of the pH of the feed and reactor contents.

The dissolved oxygen of the gas effluent from the reactor and the liquid effluent of the reactor, were originally measured using a Beckman-Process Oxygen Analyzer, model 778. The analyzer was connected to a probe located in the gas effluent line and the liquid effluent line. The probe in the liquid effluent line became unworkable because of fouling. The Beckman Dissolved Oxygen Analyzer was replaced by a Union Carbide Dissolved Oxygen Analyzer, model 1101. The Beckman unit was still used to monitor the oxygen in the effluent gas.

The feed was pumped into the reactor from a tank located after the primary settling tanks of the sewage treatment plant, by a Robins and Meyers-Moyno Pump,

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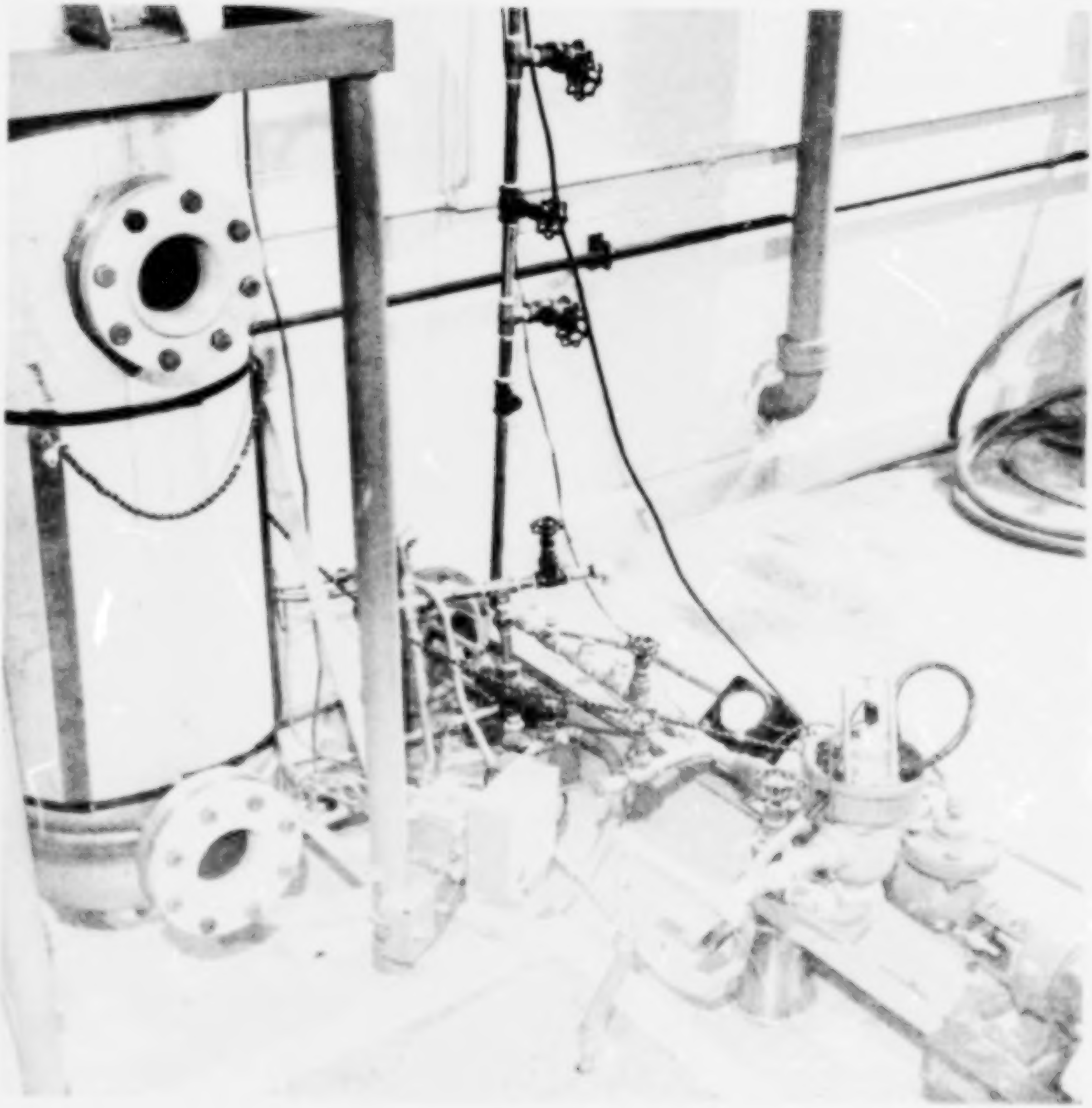
model SM2, with stainless steel construction. In order to be able to vary the feed flow rate, the pump was driven by a Vickers 3/4 horsepower hydraulic transmission, model TR8-H18-F18-29. The transmission, in turn, was powered by a General Electric 1/2 horsepower AC motor.

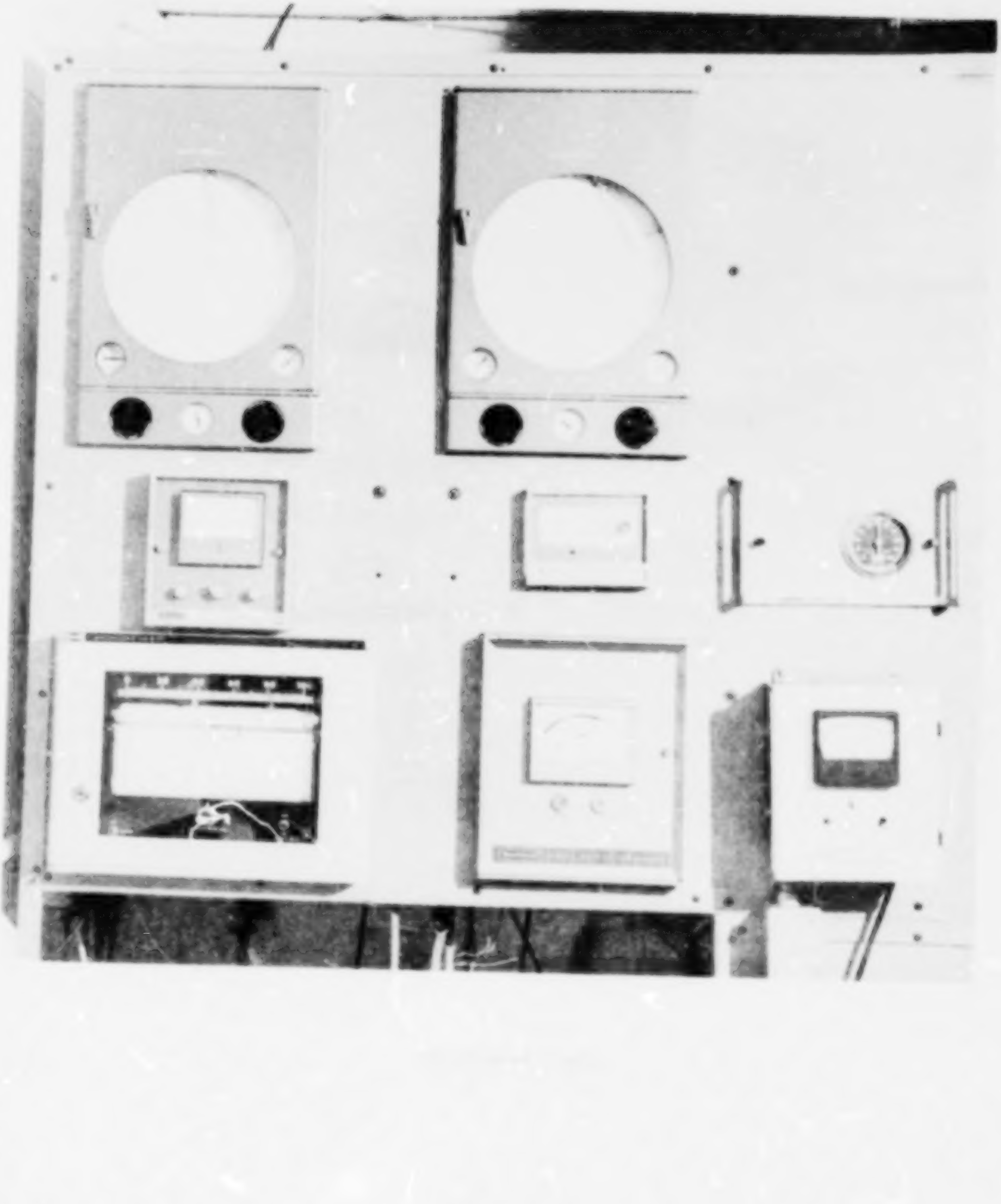
The flow rate was measured first by a Fischer & Porter rotameter, located in the feed line. But this method did not work due to fouling of the inside of the rotameter, making accurate measurement impossible. The flow rates, during most of the experimental runs, were taken by extracting a measured volume of sample in a given amount of time. The system is now equipped with a Brooks Electromagnetic flow meter and signal converter, model 7460-1. The magnetic coil is located in the feed line, just before it enters the reactor.

The reactor was operated at constant volume by keeping the level inside the reactor at a constant value with a Honeywell Recorder-Controller, model #Y702P2. A signal, proportional to the hydrostatic head in the reactor, was sent to the controller by a Honeywell Differential Pressure Transmitter. The controller could then send a signal to a Conoflow Corporation Control valve, model AB-10XM, located in the liquid effluent line.

Air, which was needed for the controllers and the sparger in the reactor, was supplied by an Ingersoll-Rand Type 30 Air Compressor, model 234. The air rate of the compressed air entering the system was measured by a Fischer & Porter rotameter. It was held at a constant value manually, by means of a valve located in the line, just after it entered the building from the compressor.

The pressure inside the reactor was controlled by a Honeywell Recorder-Controller, model #Y702P2(51)-93-111-74). This controller could send signals to a control valve located in the effluent gas line, in order to increase or decrease the amount of gas leaving the reactor.





B) Procedural and Sampling Techniques

In order to study the kinetics of the reaction taking place inside the reactor and, in turn, develop a mathematical model for the entire reactor system, certain parameters had to be studied while the reactor was in continuous operation. The parameters which were relevant to this study were temperature, pressure, residence time (flow rate), the concentrations of dissolved carbon in both the feed and effluent streams, and the concentration of sludge in the feed and effluent stream.

The reactor was run continuously for two days before data was to be taken. This would give the sludge an opportunity to reach its operating concentration. Experimental runs were made on the next two days.

The pressure and flow rate were set for each particular run. The pressure stayed constant, since it was being controlled, while the flow rate fluctuated only slightly during a run. The pH was not controlled during this study, although it remained between values of 6.8 - 7.2 during most of the runs.

Originally, the temperature was to be controlled automatically by a Honeywell controller, but the unit was often inoperative. The strip heaters around the bottom of the reactor, were controlled manually using the Variac voltage regulator referred to in the previous section. The temperature was kept between the values of 68°F - 76°F.

Previous studies on the reactor, using sodium chloride as a tracer, showed that ideal mixing was maintained if the air rate was greater than 1.43CFH.[5] The air rate was set above this level.

Samples were taken from valves located in the feed and effluent lines at least once every hour from about 8:00 a.m. until approximately 11:00 p.m. Between 9:00 - 10:00 a.m. and 2:00 - 3:00 p.m., samples were taken every fifteen minutes, since dissolved carbon concentration reached a peak during these times.

Using this sampling scheme, a good history of concentration versus time could be obtained.

The flow rate was checked at the same time a sample was being taken. Since the rotameter used for measuring the liquid flow rate was not operating and the magnetic flow meter had not yet been received, a measured volume of sample was taken in a given amount of time in order to determine the flow rate.

The samples were taken back to the laboratory to be analyzed for the dissolved carbon concentration and concentration of solids in both the feed and effluent.

C) Analysis of Samples

The samples taken of the feed and effluent were analyzed for their total carbon concentration and solid concentration. The instrument which was used to determine dissolved carbon concentrations was a Beckman Model 315 Infrared CO_2 Analyzer.

The volume of each sample was noted prior to its vacuum filtration. The suspended solids were separated from the samples and were dried and weighed. The weight of the solids plus filter paper minus the weight of the filter paper was the weight of the suspended solids. Knowing the volume of the original sample from which the solids were obtained, the concentration of solids per ml was determined.

The filtrate was analyzed for its dissolved, total carbon concentration by means of a system made up of a reaction chamber and sample injection assembly, an electronic housing containing a timer to control the sample valve operation, a meter and potentiometer to adjust and indicate the power level of the reaction chamber, and the Beckman Model 315 Infrared CO_2 Analyzer.

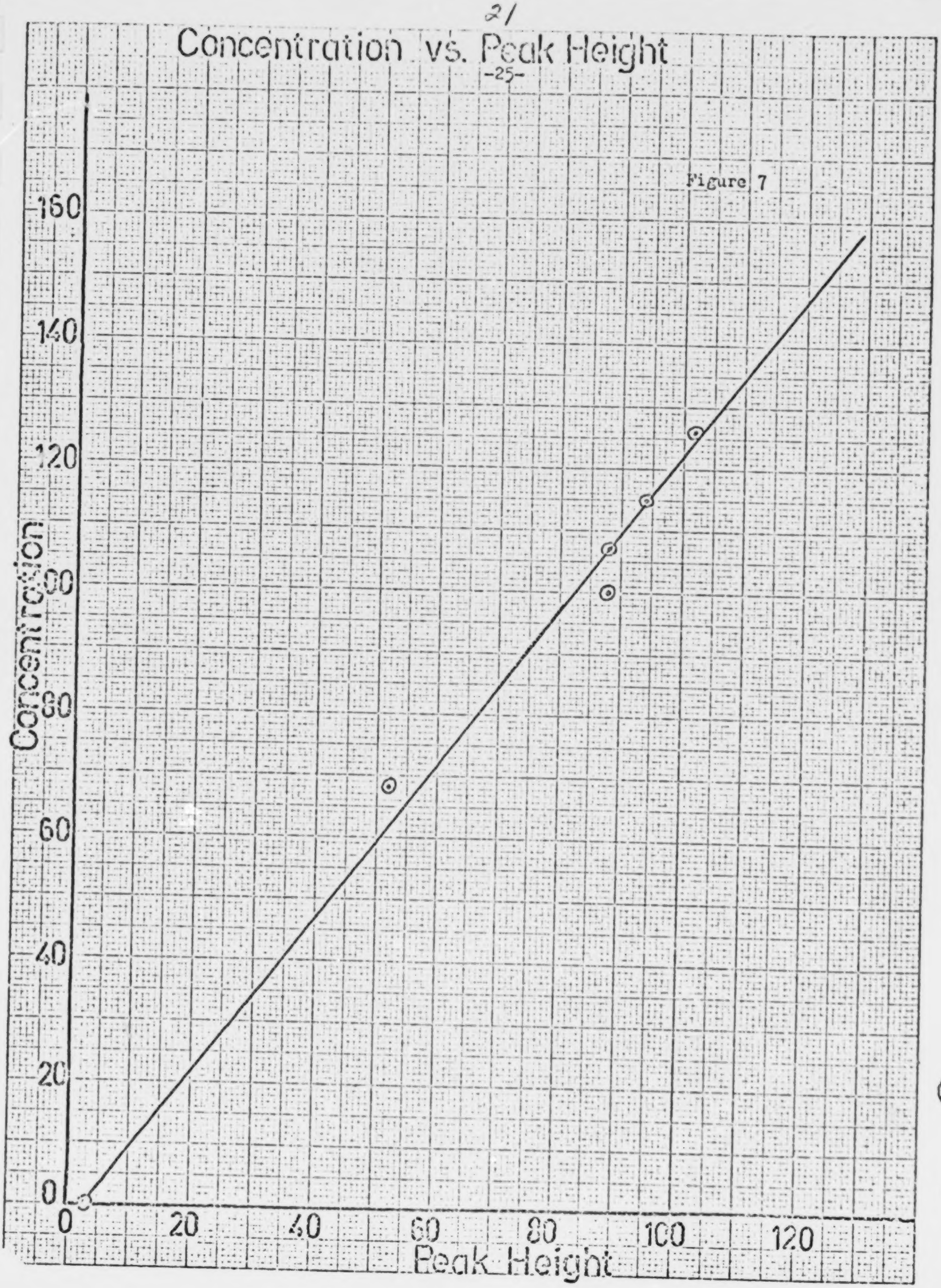
The sampling injection assembly automatically took a 40 microliter sample and injected it into a nitrogen carrier gas stream which carried it to the reaction chamber. The reaction chamber was made from Vycor tubing with a length of coiled palladium wire mounted inside. Power to the palladium was kept at 250 watts. It was inside the reaction chamber that the samples were vaporized and the organic content oxidized to CO_2 and water. The water present was then condensed out before the products reached the infrared analyzer, where the amount of CO_2 present was determined. A signal was then sent to a Leeds and Northrup recorder. A record of peak heights proportional to the amount of CO_2 present in the injected sample was thus tabulated.

A standardization curve (Figure 7) was constructed so that the peak heights on the recorder plots could be related directly to the total carbon in a sample. This was done using n-butanol and water solutions containing 20, 40, 60, and 100 milligrams of carbon per liter of solution. These standard solutions were injected into the combustion tube. The peak heights which were obtained were plotted against the total amount of carbon which was present in the samples. This curve permitted us to find the total carbon content present in a sample by the peak height output on the recorder.

D) Results of Pilot Plant Studies

The result of the experimental work at the pilot plant is represented in the form of concentration versus time graphs (Figures 15-36). These graphs present the dissolved carbon concentration history of both the feed and effluent streams. In the runs made through February 14, only the solid concentration of only the effluent stream was found. After February 16, the solid concentration was obtained in both the feed and effluent stream.

In order to obtain usable concentration data, the reactor was found to operate best at residence times not exceeding 1-2 hours. If it was operated at greater residence times, almost complete biological conversion occurred, giving little information about the output dissolved carbon concentration. For a kinetic study of any usefulness, the output concentration would have to be a significant fraction of the input concentration.


Concentration vs. Peak Height
Figure 7
Concentration
160
140
120
100
80
60
40
20
0
Peak Height
0
20
40
60
80
100
120

Due to operating under unsteady state conditions, very little could be concluded qualitatively about the effects of temperature and pressure from the graphs. Any effects would be found through a quantitative study using a mathematical model for the system.

What does seem to show some sort of pressure dependence is the sludge growth within the reactor. It can be seen from the graphs in Figures 15-36, that the amount of sludge produced decreases with an increase of pressure. Runs made at 100 psig showed, on the average, a solid concentration which was generally smaller than at pressures of 20 and 60 psig.

IV. THE MATHEMATICAL MODEL

A) The Material Balance

To analyze the reactor system mathematically, material balance equations must be written. The schematic shown in Figure 9 represents the reactor and the inputs and outputs.

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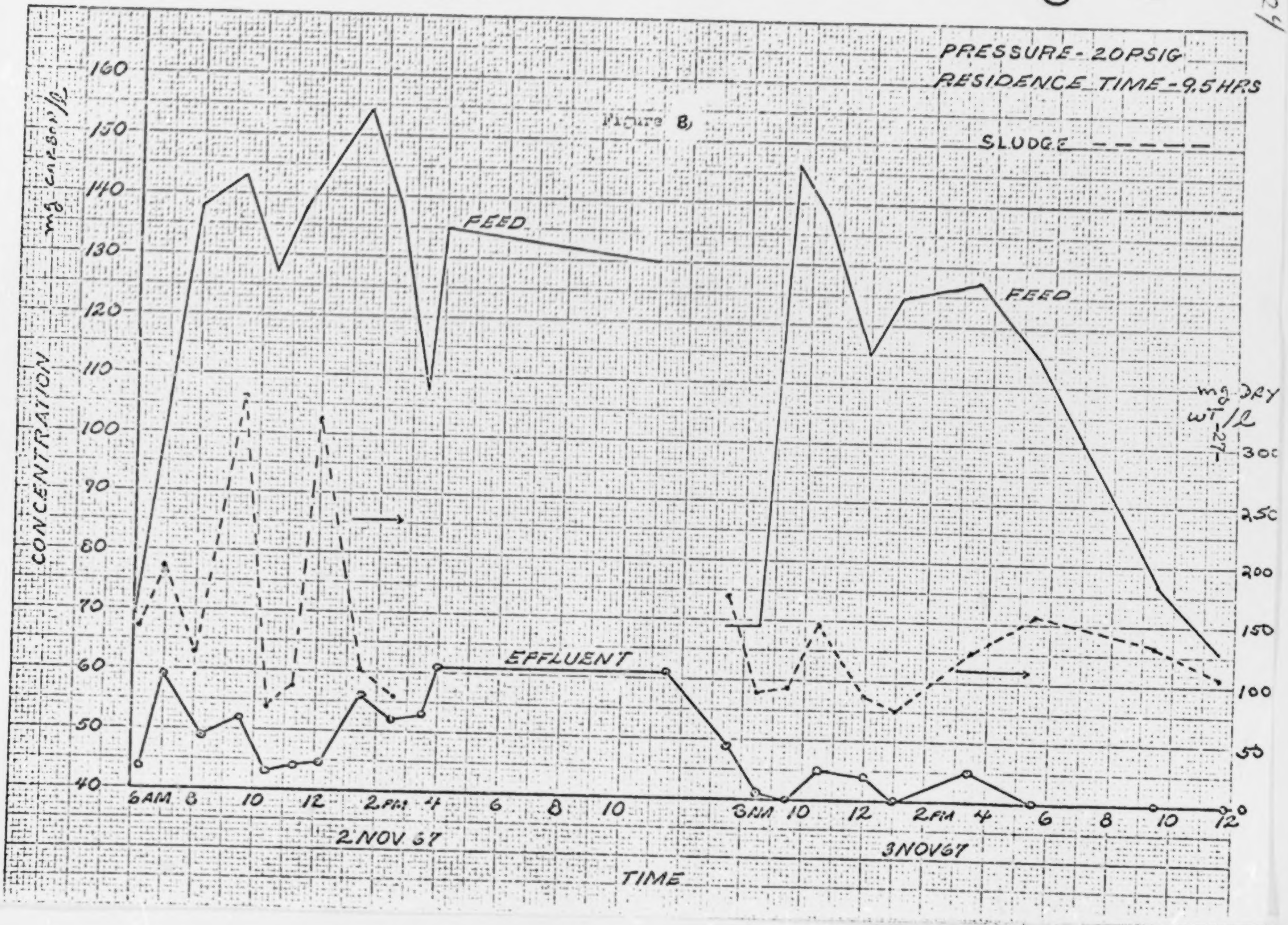

Figure 8

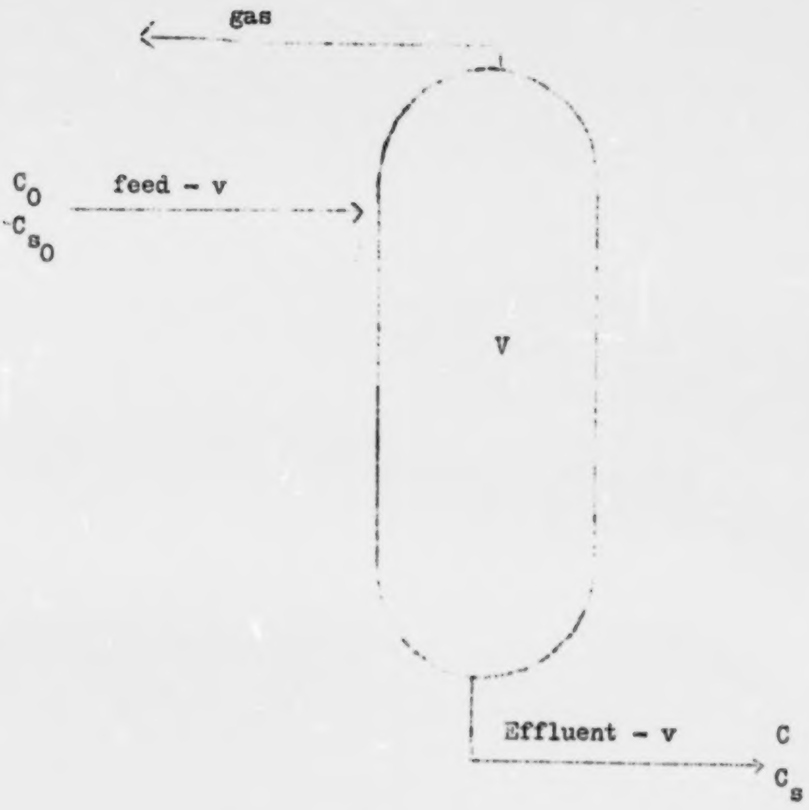

Figure 9

where:

V = volume of liquid in the reactor
C_0 = feed dissolved carbon concentration (=) mg C/L
C = effluent dissolved carbon concentration (=) mg C/L
C_s = effluent solids concentration mg C/L
C_{s_0} = feed solids concentration (=) mg C/L
v = volumetric flow rate (=) cc/min

The general form of the material balance is:

$$\begin{pmatrix}\text{Rate of}\\ \text{Mass Input}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{Mass Output}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{Disappearance}\\ \text{of Mass by}\\ \text{Reaction}\end{pmatrix} = \begin{pmatrix}\text{Accumulation}\\ \text{of Mass in}\\ \text{the Reactor}\end{pmatrix} \quad (5)$$

Applying equation (5) to a dissolved carbon balance for the reactor, equation (6) is obtained:

$$\frac{dC}{dt}V = v\,C_o - vc - R_c\,V \tag{6}$$

where:

R_c = the rate of disappearance of dissolved carbon by the biological reaction taking place within the reactor.

A similar equation is obtained for solids balance:

$$\frac{dC_s}{dt}V = v\,C_{so} - v\,C_s + R_s\,V \tag{7}$$

where:

R_s = the rate of appearance of sludge due to the biological reaction.

Equations (6) and (7) may be rewritten, rearranging terms, to give the following:

$$dC/dt = c_o/\theta - C/\theta - R_c \tag{8}$$

$$dC_s/dt = C_{so}/\theta - C_s/\theta + R_s \tag{9}$$

where:

$\theta = V/v$

There are now two equations, which, when the appropriate rate expressions are used, will describe the dynamic behavior of the activated sludge reactor being studied.

Equations (8) and (9) are valid if the following assumptions are used:

1) Since the reactor is completely mixed, the effluent concentrations are the same as those within the reactor. As previously mentioned, this assumption was proven to be valid.

2) The volumetric flow rate is a constant throughout the reactor system, since the density is assumed constant.

These equations may now be used to analyze the experimental data and determination of the reaction kinetic models.

B) The Rate Expression

As previously discussed, there are different views regarding the kinetics which describe the reactions which take place in biological systems of the type being studied in this work. A chart has been prepared showing the various proposed kinetic models and the constants associated with each of them (Table 1).

It was our intention to take some of the better known kinetic expressions for the rate of disappearance of dissolved carbon and arrive at the one which fit the experimental data the best.

The Michaelis-Menten expression (equation 10) was chosen to represent the rate of disappearance of dissolved carbon.

$$R_c = \frac{HCC_s}{T + C} \tag{10}$$

This expression, which has been discussed earlier in this report, has been accepted by many researchers in the area of biological kinetics.

The rate expression for the rate of appearance of activated sludge will be of the same form as Equation 10. So only the values of the reaction rate constants will be different.

V. ANALYSIS OF EXPERIMENTAL DATA

A) Computer Analysis - Continuous System Modeling Program (CSMP)

In order to determine the reaction rate constants in the proposed reaction rate equations, the experimental data had to be analyzed using the mathematical model equations. An IBM 360 computer was used for this purpose. The computer at the University of Connecticut was equipped with a language known as the Continuous Systems Modeling Program - CSMP, which saved much work in the analyzing of the differential equations describing the activated sludge system.

The method used was to find the values for the reaction rate constants, which when used in the mathematical model equations, (8 and 9), gave the best fit for the experimental data. The procedure followed by the program was to calculate values for the effluent concentration C, in the case of the total carbon balance, and Cs, in the case of the sludge balance, using the experimental data for each run. Arbitrary values of the reaction rate constants were used to start the run.

The sludge concentration in the feed, for the runs made from November 2 through February 14, was not taken and so an average sludge concentration graph was drawn for this period (Figure 10). This was done using the results from February 16 on. Averages were taken at each time of sampling and a complete average history was formed.

As each effluent concentration was calculated, it would be compared to the value of the effluent concentration determined experimentally to arrive at the error between the two. The error function used for this comparison is shown in Equation 11.

$$\text{error} = \sum_{i=1}^{N} (C_i\text{exp} - C_i)^2 \qquad (11)$$

where:

N = number of data points in run

The value of the error of the entire experimental run would then be analyzed by a two parameter search, written by Alan Molvar, a Ph.D. candidate in the Chemical Engineering department. This part of the entire program would compare the value of the error function against its previous value. It would then adjust the values of the reaction rate constants, depending on whether or not the error had increased or decreased since the previous run. After altering the values of the constants, the computer began again to determine a new value for the error function. This would continue until the lowest value of the error function was found, signifying the best values of the reaction rate constants.

A copy of the programs for both the total carbon and sludge balances (Equations 8 and 9) appear in the appendix. The two parameter search was not

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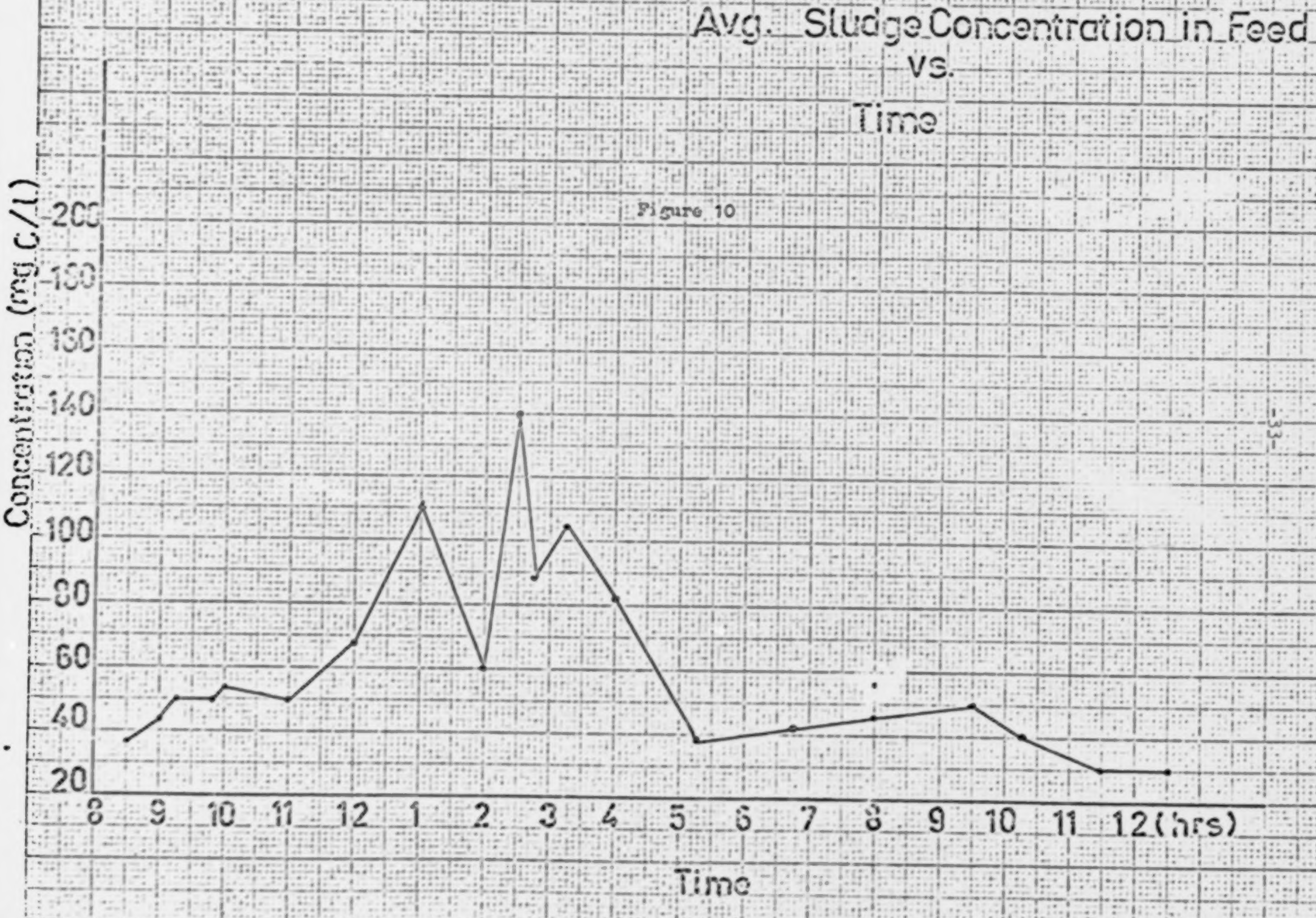

Figure 10

used in the program for the sludge balance since the results of the determination of the reaction rate constants for the total carbon balance showed it not too necessary.

Figure 11 shows how the calculated total carbon concentration in the reactor compares with experimental data.

B) Error Curves for Michaelis-Menten Constants

It was expected that the result of the two parameter search would be the determination of one set of reaction rate constants which, when used in the mathematical model equation, would give the smallest error between the calculated effluent concentration and the experimental value. This turned out not to be the case.

The results of the computer study are shown as plots of the constant H versus T (Figures 37-61 in the appendix) for each experimental run. The curves represent the lines of constant error.

It was found that, no matter where the pattern search was started, eventually the values of the constants H and T appeared on a ridge line of almost constant error. The value of the error along this ridge curve was lowest for each particular run. It was concluded that as long as the combination of the reaction rate constants, H and T, lay along this ridge curve, they gave approximately the best fit for the experimental data.

C) Rate Constants for the Production of Sludge

The rate expression for the rate of production of sludge was discussed previously as taking on the same form as the expression used for the rate of removal of carbon. The results of the study of the total carbon balance would thus determine the reaction rate equation for the production of sludge. It was mentioned now, for the understanding of the analysis technique, that it was found that the reaction rate equation for the disappearance of total carbon was

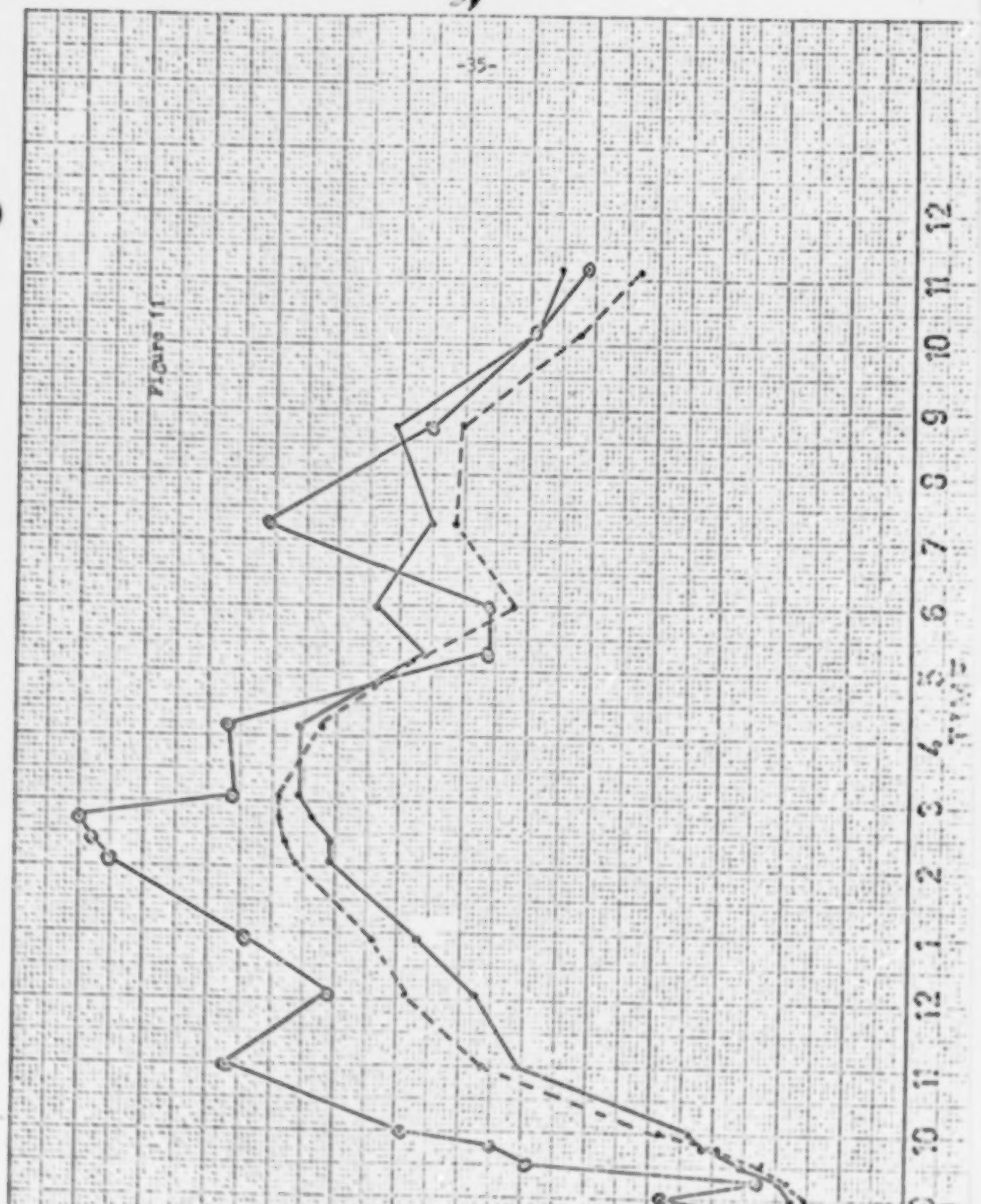
Figure 11
Concentration (mg/l)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Time
8
9
10
11
12
1
2
3
4
5
6
7
8
9
10
11
12

second order if the proper choice of the constants, H and T, was made. Thus a second order equation was used for the computer analysis of the sludge balance. The equation used for the rate equation had the following form:

$$r_s = k_B C C_s \tag{12}$$

where:

k_B = the rate constant for the production of sludge

Since only one constant appears in this equation, the two parameter search used to determine the constants H and T was not needed. Instead, a method of finding the value k which gave the best fit for the experimental data was needed.

The error function shown in equation 11 was used again to find the value of the constant which gave the smallest value for it. Plots were of the error versus the reaction rate constants (Figures 62-81 in the appendix) were made. The point at which the error function was set at a minimum value was also the value of k wanted. The values of k for each experimental run are listed in Table 2.

Table II

Date		Pressure (psig)	K_b (L/hr. mg carbon)	(K_o-K_b) (L/hr. mg carbon)	Y (mg sludge/mg carbon)
Nov.	2	20	—	—	—
	3	20	$.44X10^{-3}$	$.96X10^{-3}$	.31
	8	20	—	—	—
	9	20	$2.1X10^{-3}$	$.74X10^{-3}$	.74
	15	20	$2.7X10^{-3}$	—	—
	16	20	$1.7X10^{-3}$	$.15X10^{-3}$	.92
	21	20	$.88X10^{-3}$	—	—
	22	20	—	—	—
	29	20	$.70X10^{-3}$	—	—
	30	20	—	—	—
Dec.	6	0	$1.7X10^{-3}$	$.15X10^{-3}$	.92
	7	0	$4.6X10^{-3}$	—	—
	13	0	—	—	—
Jan.	5	60	—	—	—
	10	60	$1.15X10^{-3}$	$.52X10^{-3}$	.69
	11	60	—	—	—
Feb.	13	100	—	—	—
	14	100	—	—	—
	16	100	$.13X10^{-3}$	$2.9X10^{-3}$	.043
	27	100	$.11X10^{-3}$	$2.7X10^{-3}$	.039
Mar.	19	40	$.39X10^{-3}$	$1.5X10^{-3}$	.20
	20	40	$.01X10^{-3}$	$1.79X10^{-3}$	.0067
	26	40	—	—	—
	27	40	—	—	—
May	1	80	$.40X10^{-3}$	$1.1X10^{-3}$	.27
	2	80	$.58X10^{-3}$	$.70X10^{-3}$	.43
	7	80	$1.2X10^{-3}$	$1.2X10^{-3}$	0.0
	8	80	—	—	—

IV. RESULTS

The error curves (Figures 37-61 in the appendix), plotted from the results of the computer study of the total carbon balance, yielded several interesting facts. As previously stated, combinations of H and T which gave approximately the same minimum error were found to form a ridge curve. It was also found that the rate expression could be reduced from the Michaelis-Menten form to second order, with the proper combination of H and T.

The denominator of equation (10) consists of the sum of T and the concentration of the total dissolved carbon. When T becomes large, C no longer has much of an effect on the value of the sum. Thus the expression becomes second order:

$$\lim_{T \to \text{Large}} R_s = (H/T)\, C\, C_s = k_c\, C\, C_s \qquad (13)$$

In order to determine the value of k_c, plots of (H/T), along the ridge curve, versus T were constructed (Figures 82-103 in the appendix). The ratio H/T, approached asymptotically a constant value as the value of T increased. It was this value which was taken to be k_c. Table 3 lists the values of k_c for each experimental run.

The only benefit to using second order kinetics, instead of Michaelis-Menten kinetics, is simplicity. Instead of requiring two constants, only one is required while still obtaining the same accuracy between the model response and the system response.

Determination of the effects of temperature and pressure upon the overall reaction was accomplished by assuming it to be two reactions taking place simultaneously.

These two reactions are:

$$\text{Organic waste} + O_2 \xrightarrow{\text{sludge-}\ k} H_2O + CO_2 \qquad (14)$$

$$\xrightarrow{\text{sludge-}\ k_b} \text{New sludge} \qquad (15)$$

The reaction rate constant for the complete oxidation is k, and the reaction rate constant for the synthesis reaction is k_b. The constant, k_c, found from the total carbon balance, was the reaction rate constant for the overall sum of (14) and (15). Therefore:

$$k_c = k + k_b$$
$$k = (k_c - k_b) \qquad (16)$$

An attempt was made to study the affect of temperature k_c. It was assumed that if k_c was dependent on temperature, the following Arrhenius equation would hold:

$$k_c = k_o\ e^{-E/TR} \qquad (17)$$

Table III

Date	Pressure (psig)	K_c (L/hr. mg sludge)
Nov. 2	20	.00150
3	20	.00140
8	20	.0010
9	20	.00284
15	20	.00226
16	20	.00185
21	20	—
22	20	.00450
29	20	—
30	20	.0080
Dec. 6	0	.00185
7	0	.00156
13	0	.00250
Jan. 5	60	.00280
10	60	.00167
11	60	.00180
Feb. 13	100	.00476
14	100	.00240
16	100	.0030
27	100	.00280
Mar. 19	40	.00190
20	40	.00180
26	40	.00330
27	40	—
May 1	80	.00150
2	80	.00135
7	80	.00120
8	80	—

A plot of log k_c versus 1/T was made and no trend with temperature was observed (Figure 12). The temperature range in most of the experimental runs did not change more than ten degrees Fahrenheit, the average temperature being 72 degrees Fahrenheit. Because no predictable effect of temperature on k_c could be obtained, no temperature dependence was assumed.

It was also seen from Figure 12 that the pressure had little effect on the overall rate constant for the removal of carbon. Therefore, if the sludge concentration was maintained constant by adequate sludge recycle, there would be little advantage to operating at higher pressures if only the rate of carbon removal is considered.

The average value of k_c in Table 3 was 0.00248 1/hr. mg sludge and was subject to wide error.

The oxidation rate constant k, for the production of CO_2, was plotted against the pressure and the results are shown in Figure 13. As the pressure increases so does the value of k. This indicates that the complete oxidation reaction to CO_2 increases in importance with an increase in pressure. Therefore, as the pressure is increased, less activated sludge is produced per amount of dissolved carbon consumed. The constant, Y, previously defined as the weight of sludge produced / weight of dissolved carbon consumed, becomes:

$$Y = k_b/k_c = \frac{\text{mg sludge produced}}{\text{mg carbon consumed}} \qquad (18)$$

In Figure 14 the log of Y was plotted against pressure. As the pressure was increased Y decreased, indicating less activated sludge was being produced. The decreased production of activated sludge as the pressure increased may be of practical interest to plants where the removal and disposal of sludge is a problem. Ideally a plant should be operated to keep the rate of sludge production equal to the rate of sludge losses from sedimentation and biological death. Such a condition is obtained in practice in activated sludge systems which are coupled to a membrane filtration loop.[34]

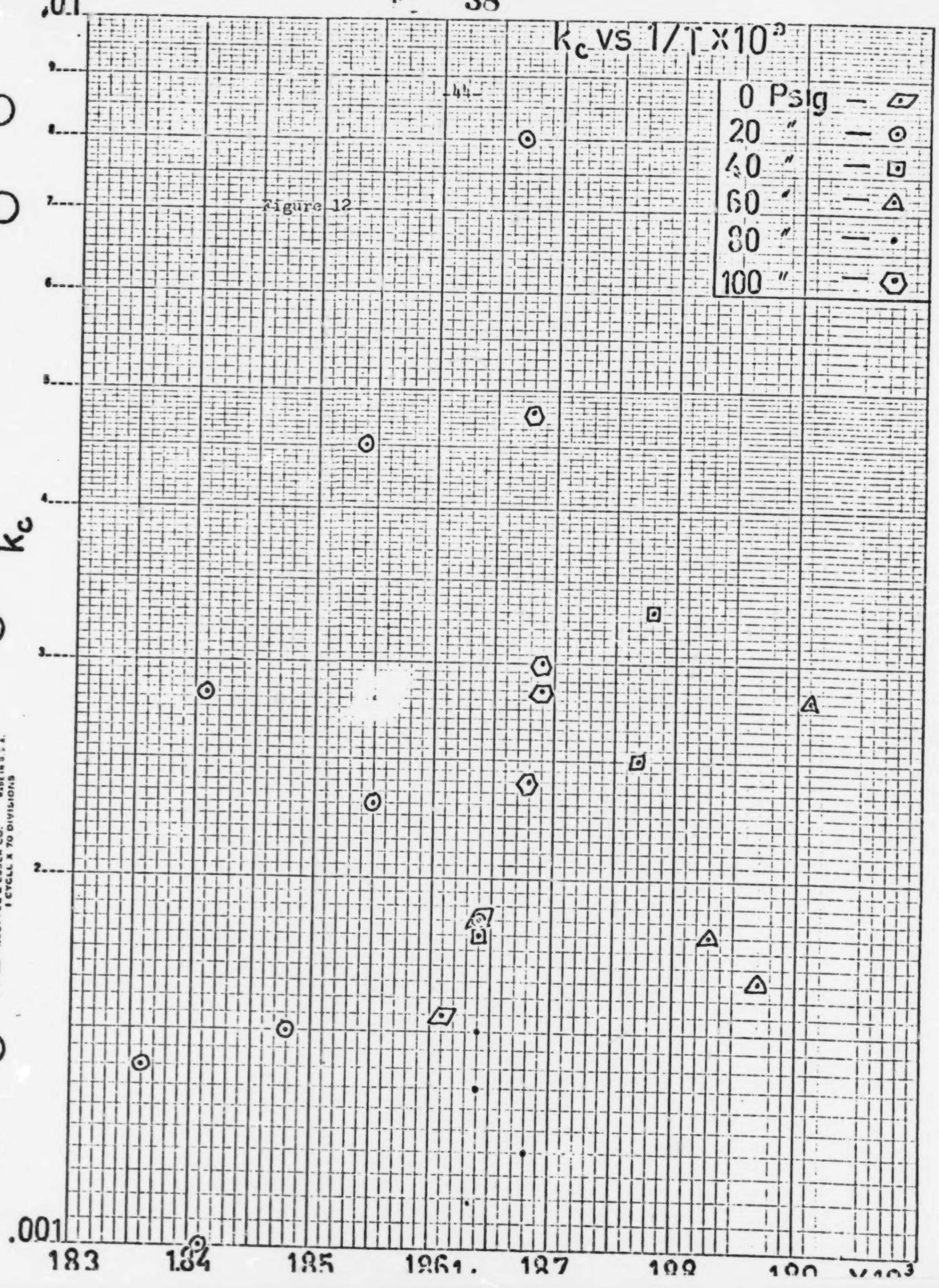
.01
k_c vs $1/T \times 10^3$
0 Psig
20 "
40 "
60 "
80 "
100 "
9
8
7
6
5
4
3
2
k_c
.001
183
184
185
186
187
188
189
190
$\times 10^3$
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Figure 12

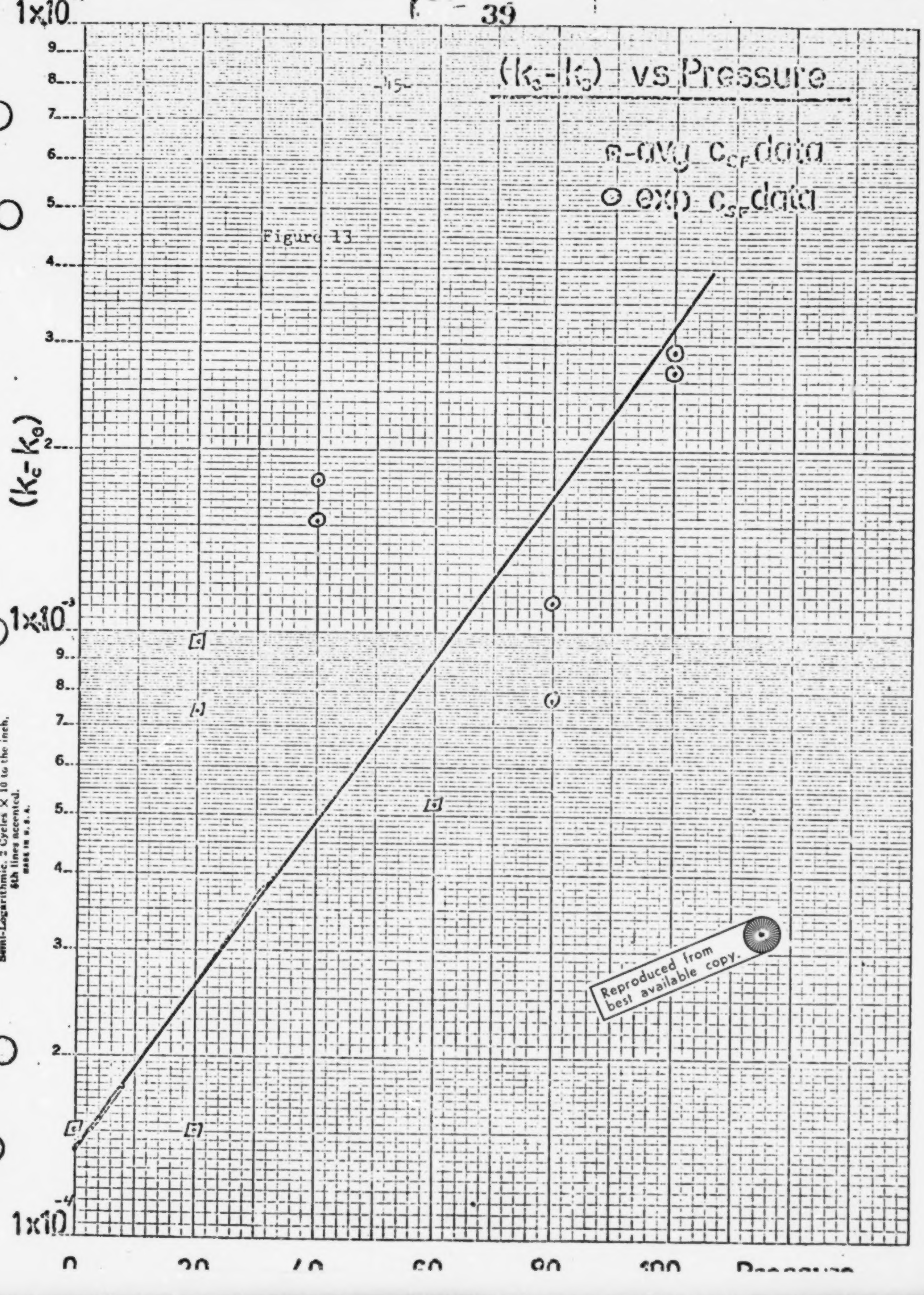

Figure 13

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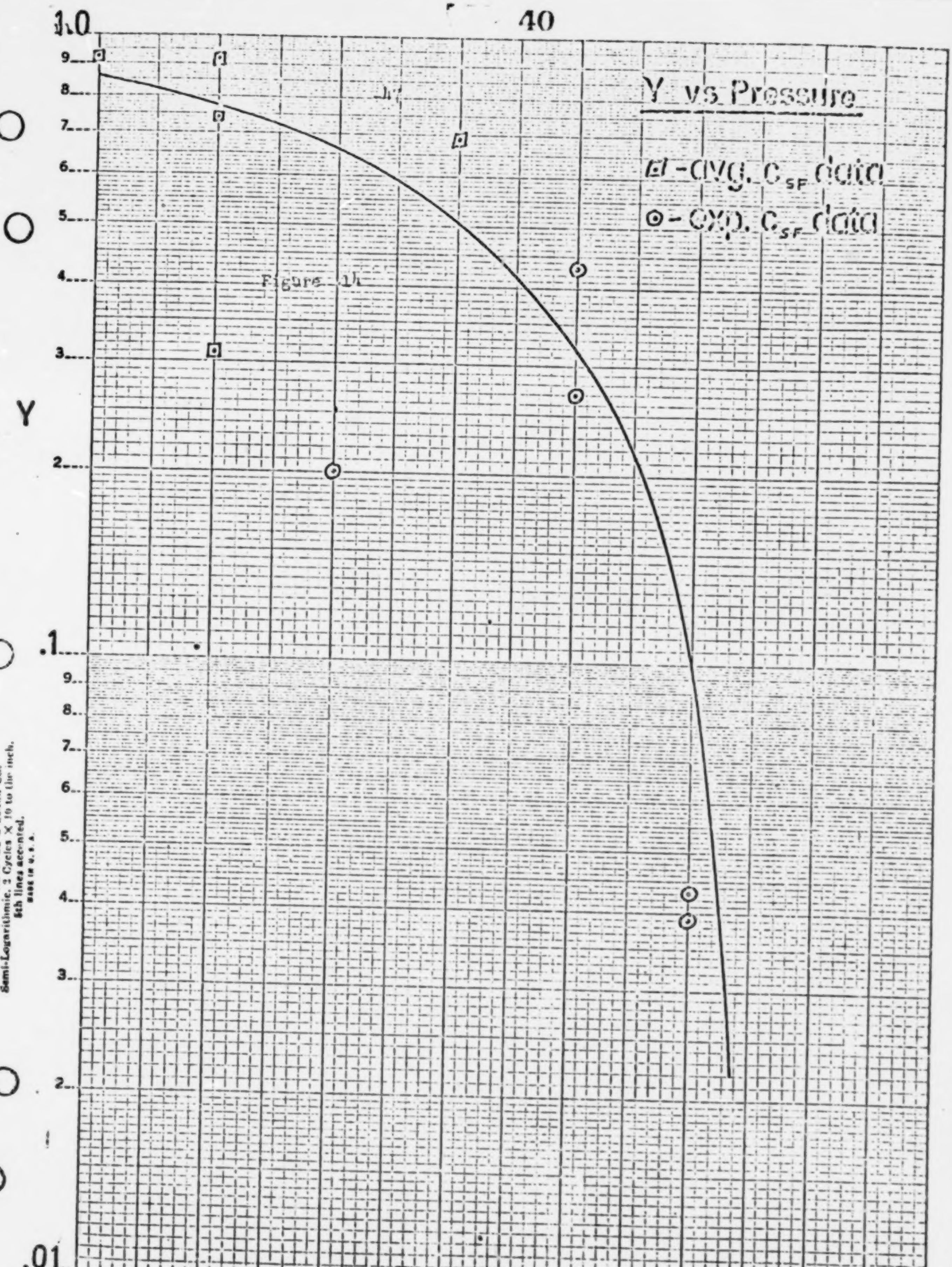
Y vs Pressure
⊡ - avg. c_SF data
⊙ - exp. c_SF data
Figure 14
Y
1.0
9
8
7
6
5
4
3
2
.1
9
8
7
6
5
4
3
2
.01
0
20
40
60
80
100
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VI. CONCLUSION

A second order reaction rate expression can be used with the same accuracy as the popular Michaelis-Menten expression, to describe the kinetics of the activated sludge reactor when it is subjected to concentration upsets.

As the pressure increased, the value of the rate constant for CO_2 production, k, increased while Y decreased, producing less sludge .

The oxidation reaction rate constant for carbon consumption was relatively independent of pressure and temperature.

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ACKNOWLEDGMENT

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APPENDIX

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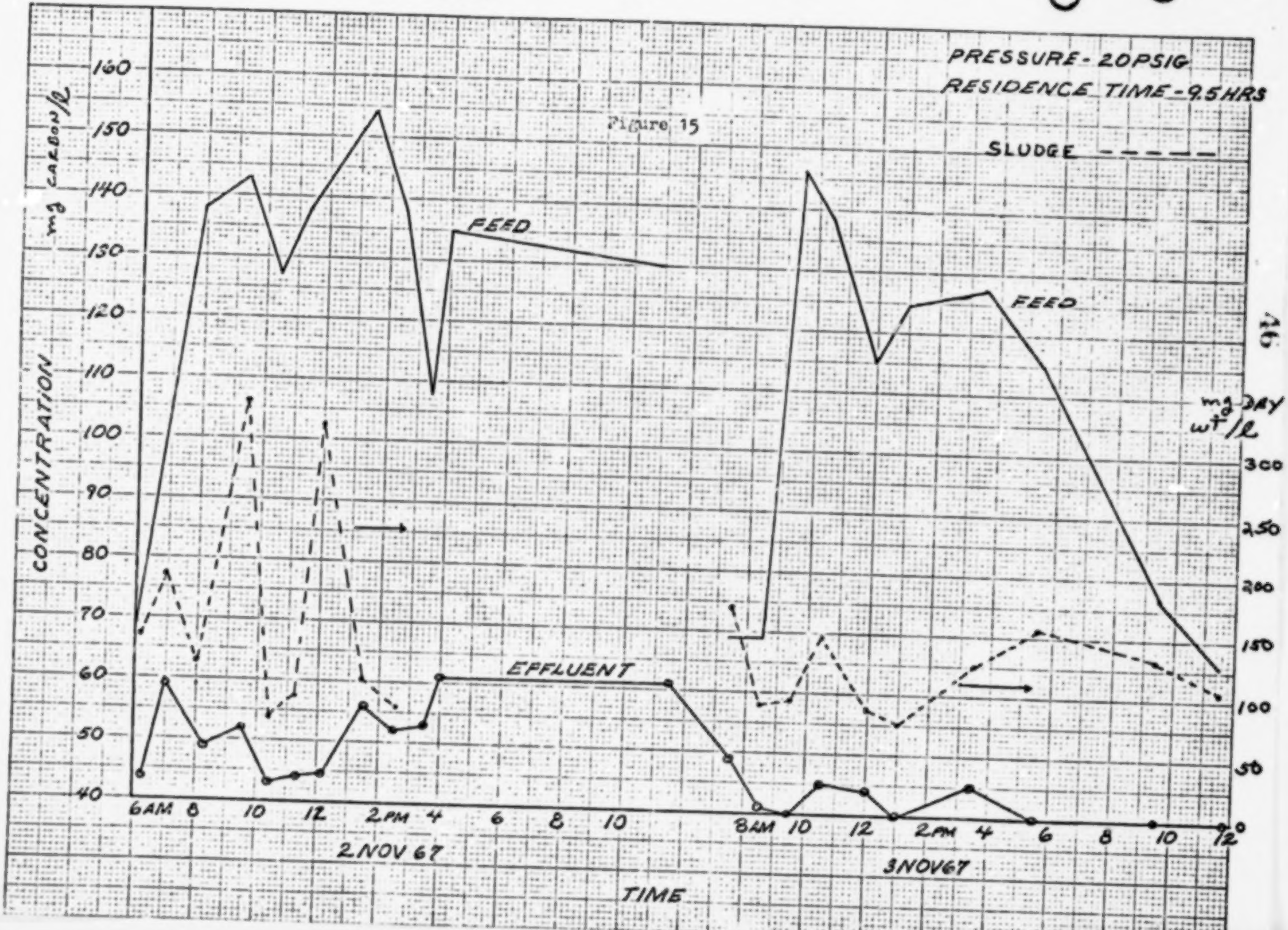


Figure 15

K+E 10 X 10 TO ½ INCH 7½ X 10 INCHES 46 1470 MADE IN U.S.A.
KEUFFEL & ESSER CO.

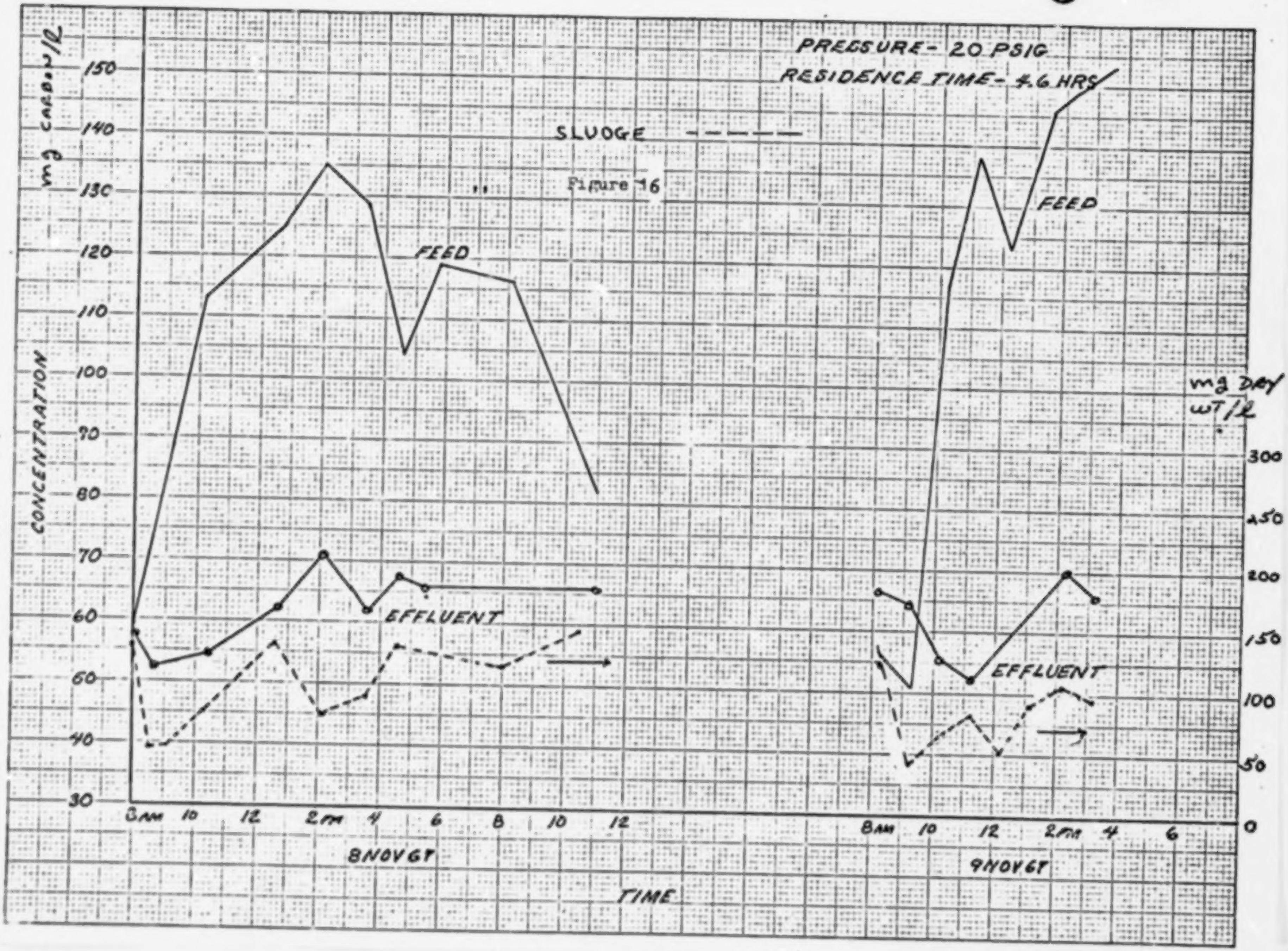


Figure 16

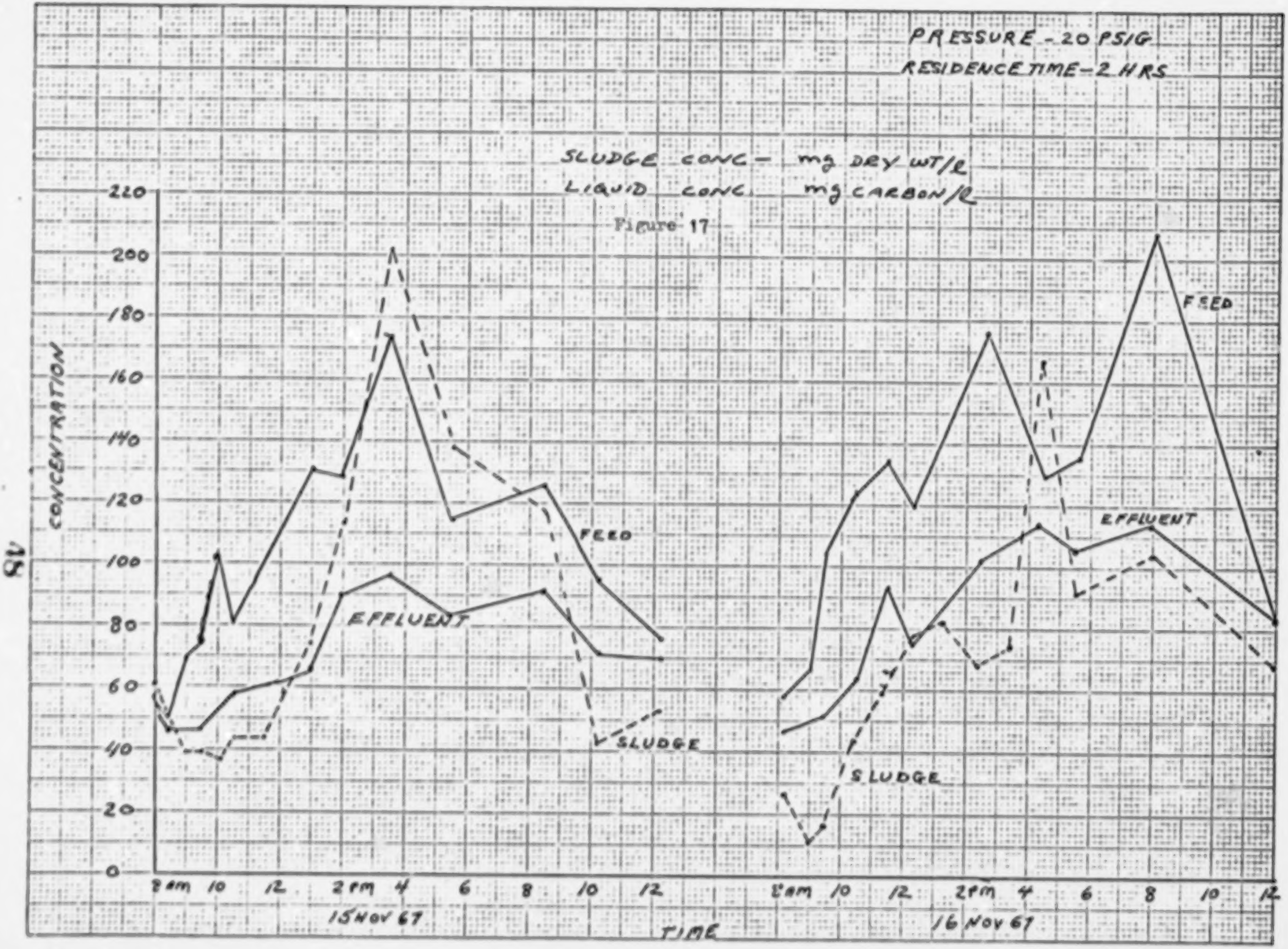


Figure 17

PRESSURE - 20 PSIG
RESIDENCE TIME - 2 HRS
SLUDGE CONC - mg DRY WT/l
LIQUID CONC. mg CARBON/l
CONCENTRATION
220
200
180
160
140
120
100
80
60
40
20
0
FEED
EFFLUENT
SLUDGE
FEED
EFFLUENT
SLUDGE
8am
10
12
2pm
4
6
8
10
12
15 NOV 67
8am
10
12
2pm
4
6
8
10
12
16 NOV 67
TIME

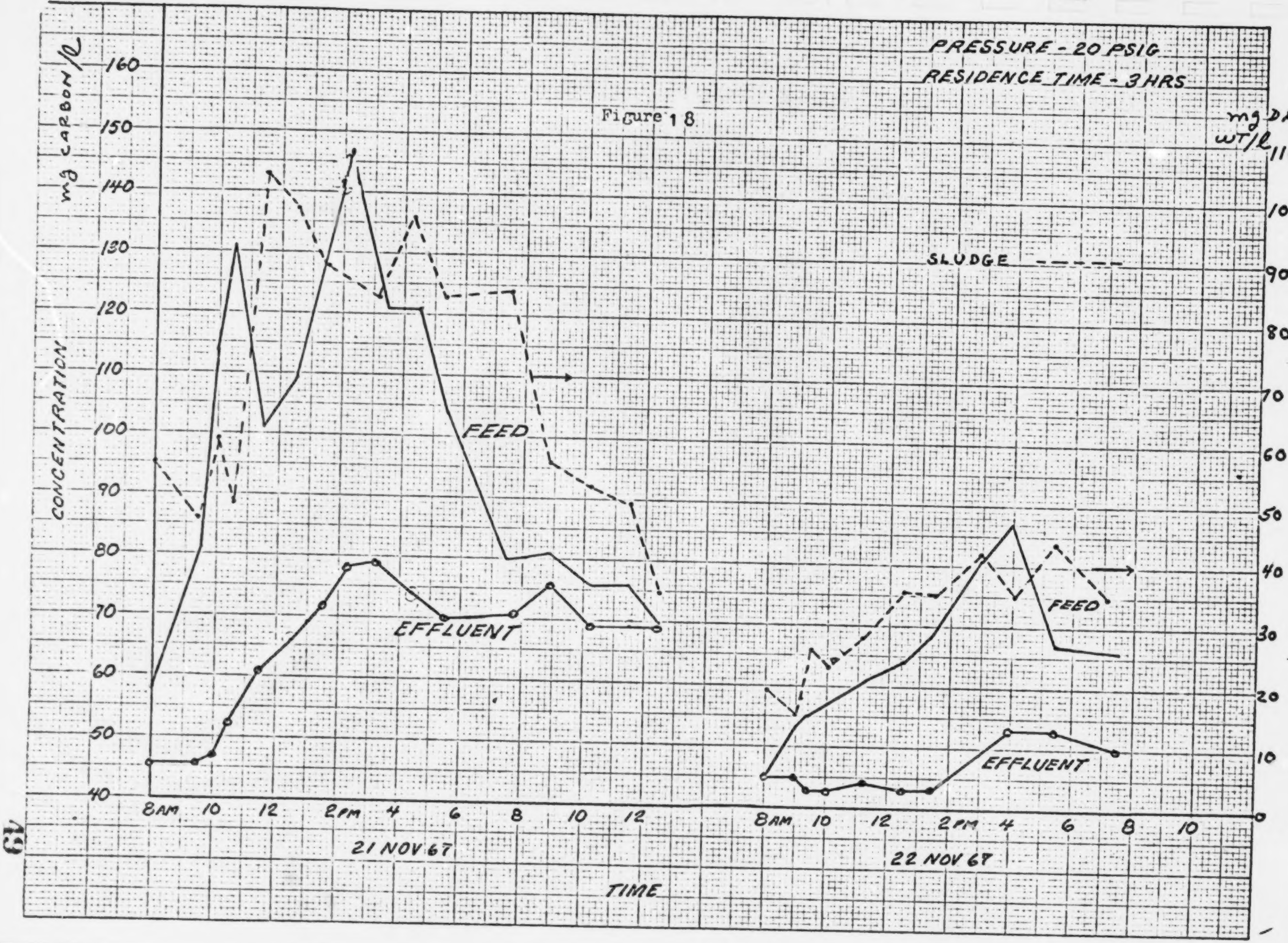


Figure 18

PRESSURE - 20 PSIG
RESIDENCE TIME - 3 HRS
mg CARBON/l
CONCENTRATION
40
50
60
70
80
90
100
110
120
130
140
150
160
mg DRY WT/l
0
10
20
30
40
50
60
70
80
90
100
110
SLUDGE
FEED
EFFLUENT
FEED
EFFLUENT
8AM
10
12
2PM
4
6
8
10
12
21 NOV 67
8AM
10
12
2PM
4
6
8
10
22 NOV 67
TIME

10 X 10 TO ½ INCH 46 1470
KEUFFEL & ESSER CO.

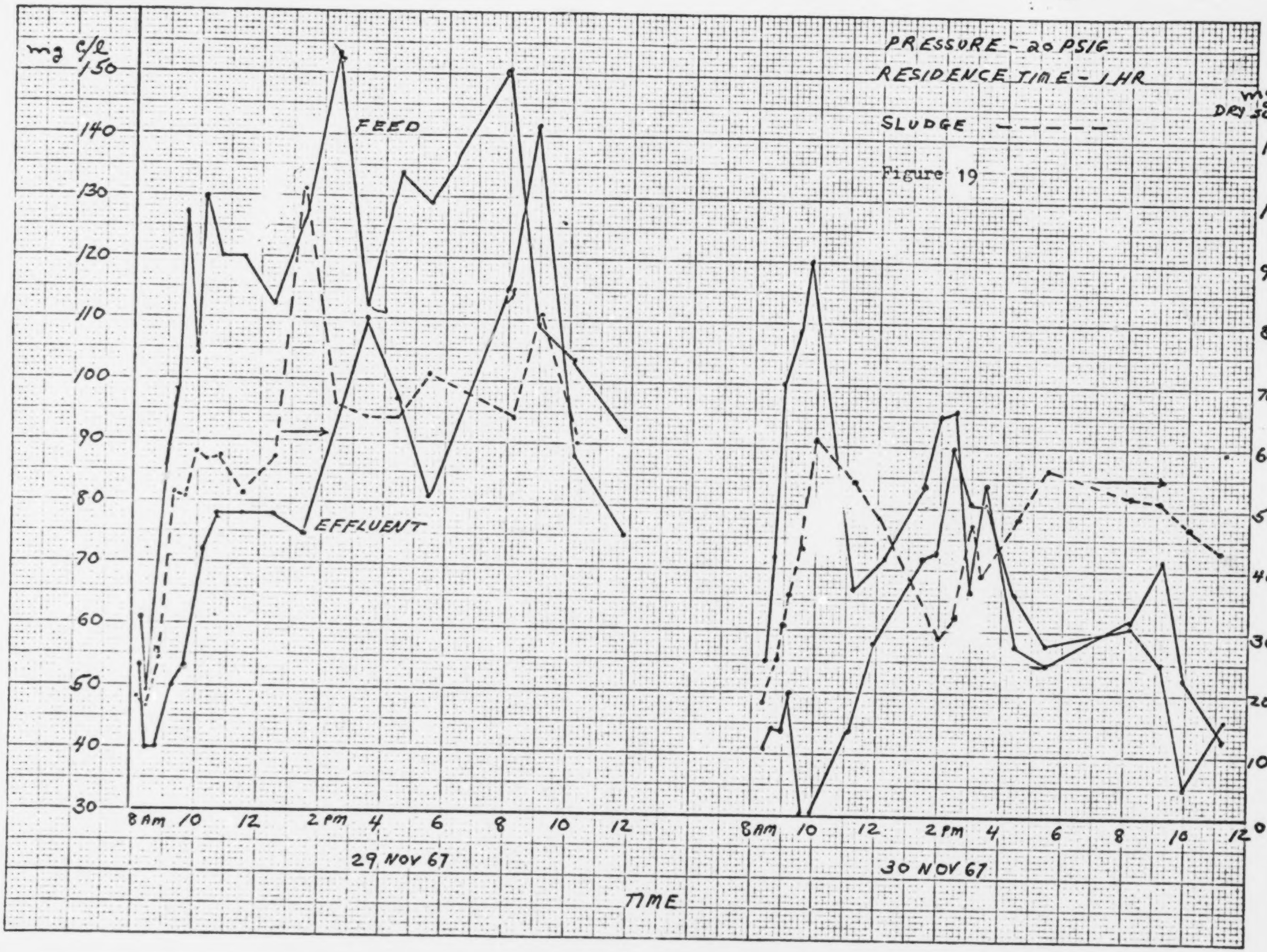


Figure 19

7½ X 10 INCHES 4 70 MADE IN U.S.A.
KEUFFEL & ESSER CO.

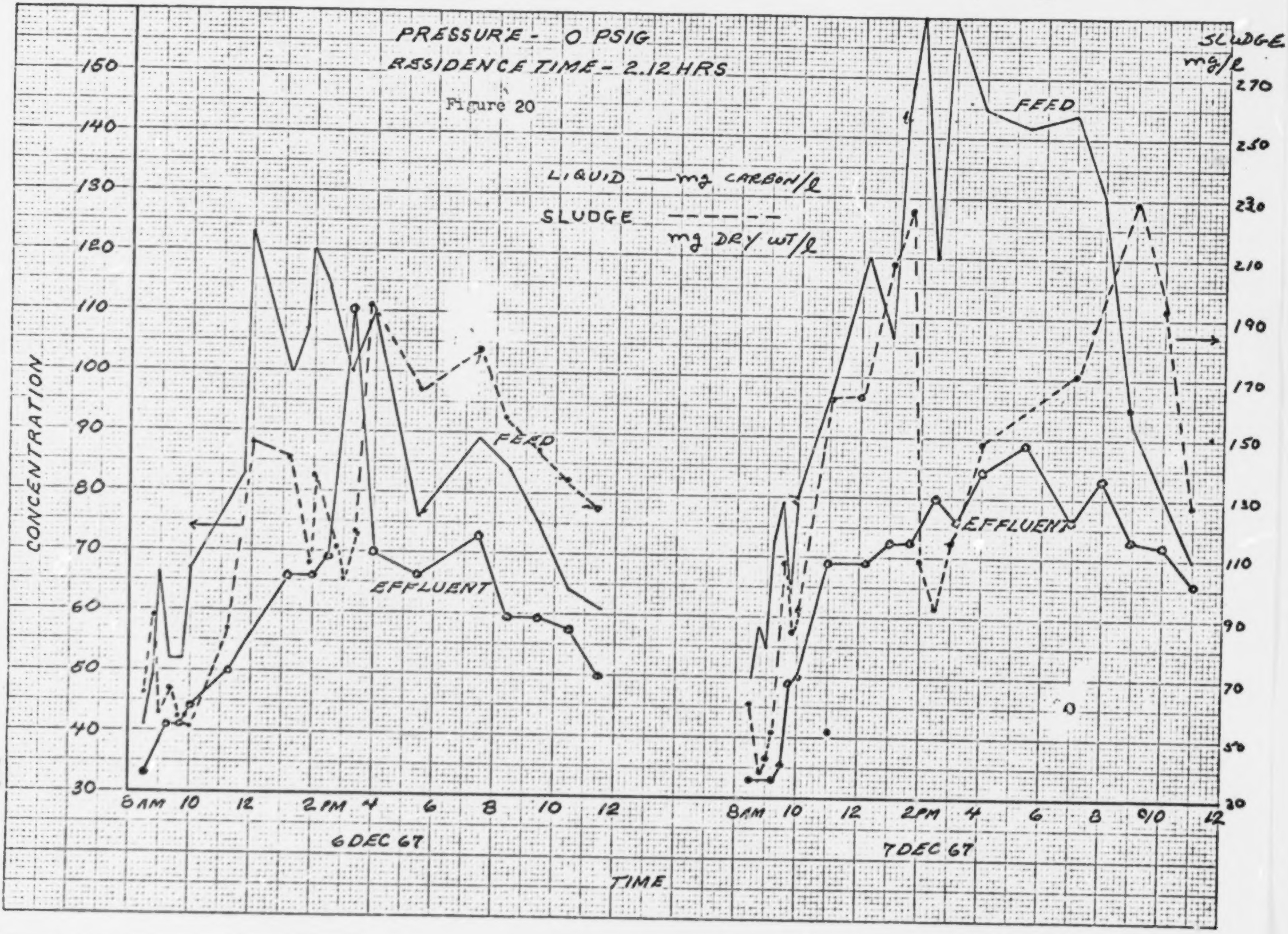


Figure 20

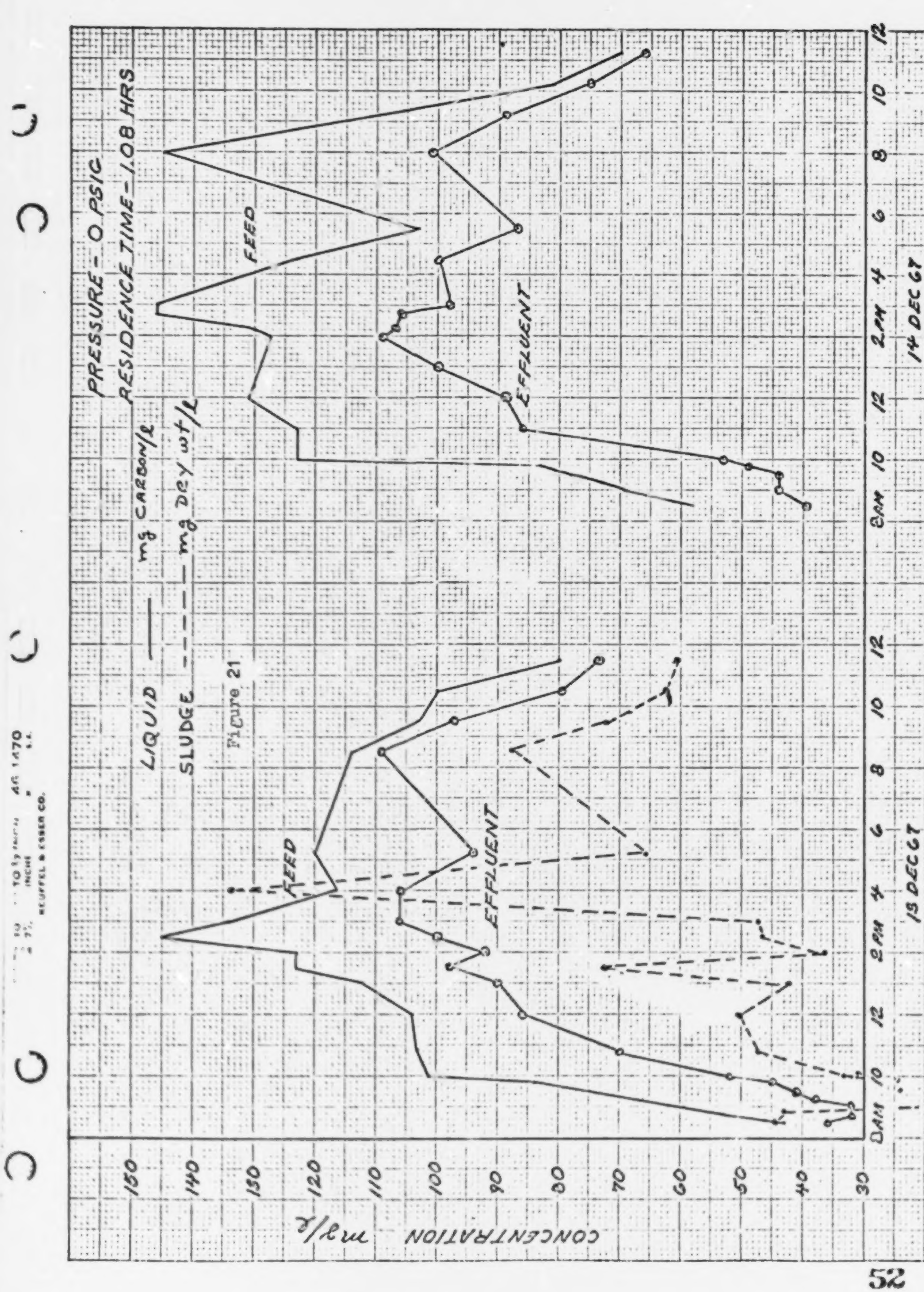
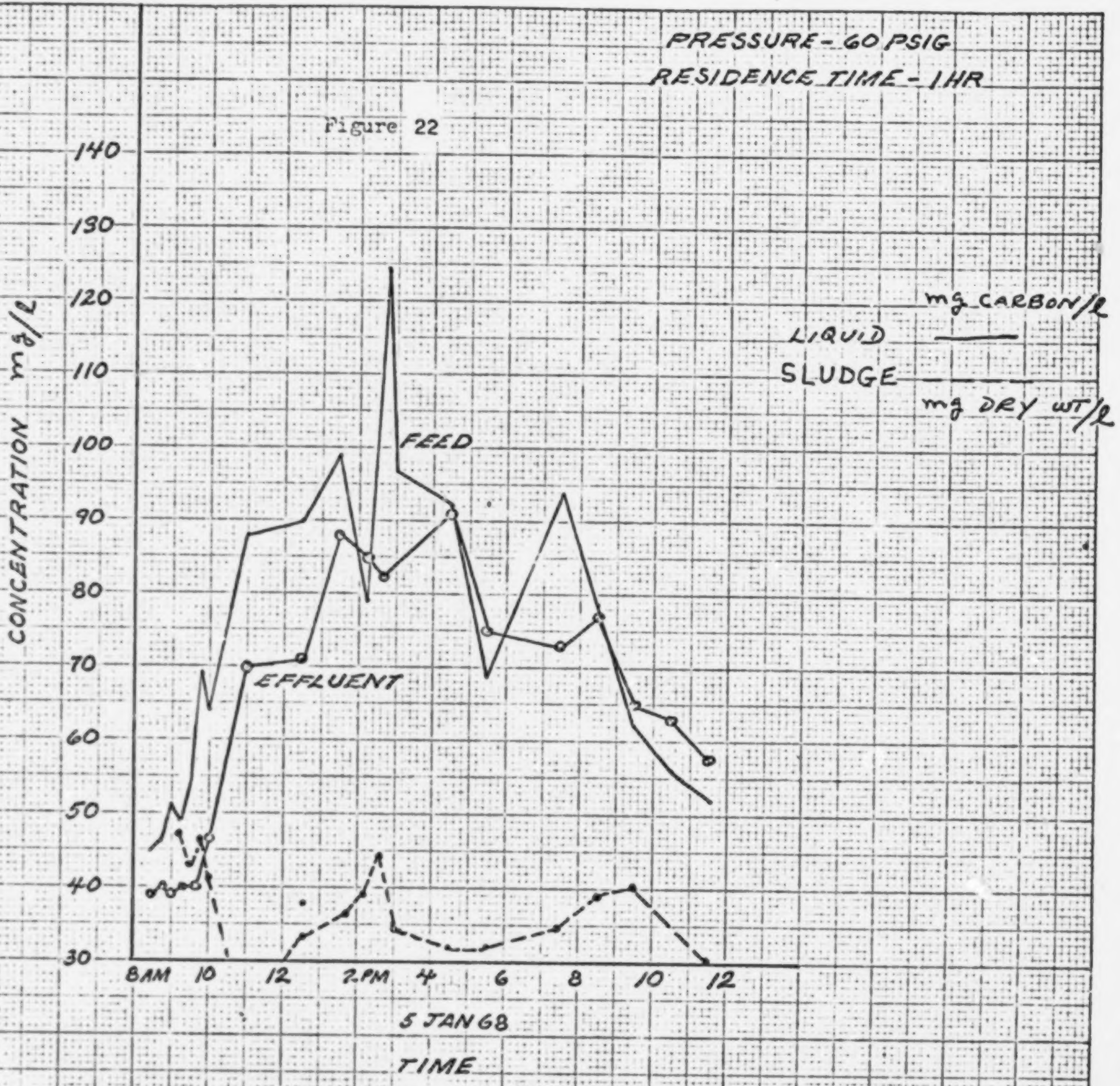


Figure 21

PRESSURE - O PSIG
RESIDENCE TIME - 1.08 HRS
LIQUID —— mg CARBON/l
SLUDGE - - - - mg DRY wt/l
FEED
EFFLUENT
FEED
EFFLUENT
CONCENTRATION mg/l
150
140
130
120
110
100
90
80
70
60
50
40
30
8AM
10
12
2PM
4
6
8
10
12
13 DEC 67
8AM
10
12
2PM
4
6
8
10
12
14 DEC 67
TIME

KEUFFEL & ESSER CO.

Figure 22



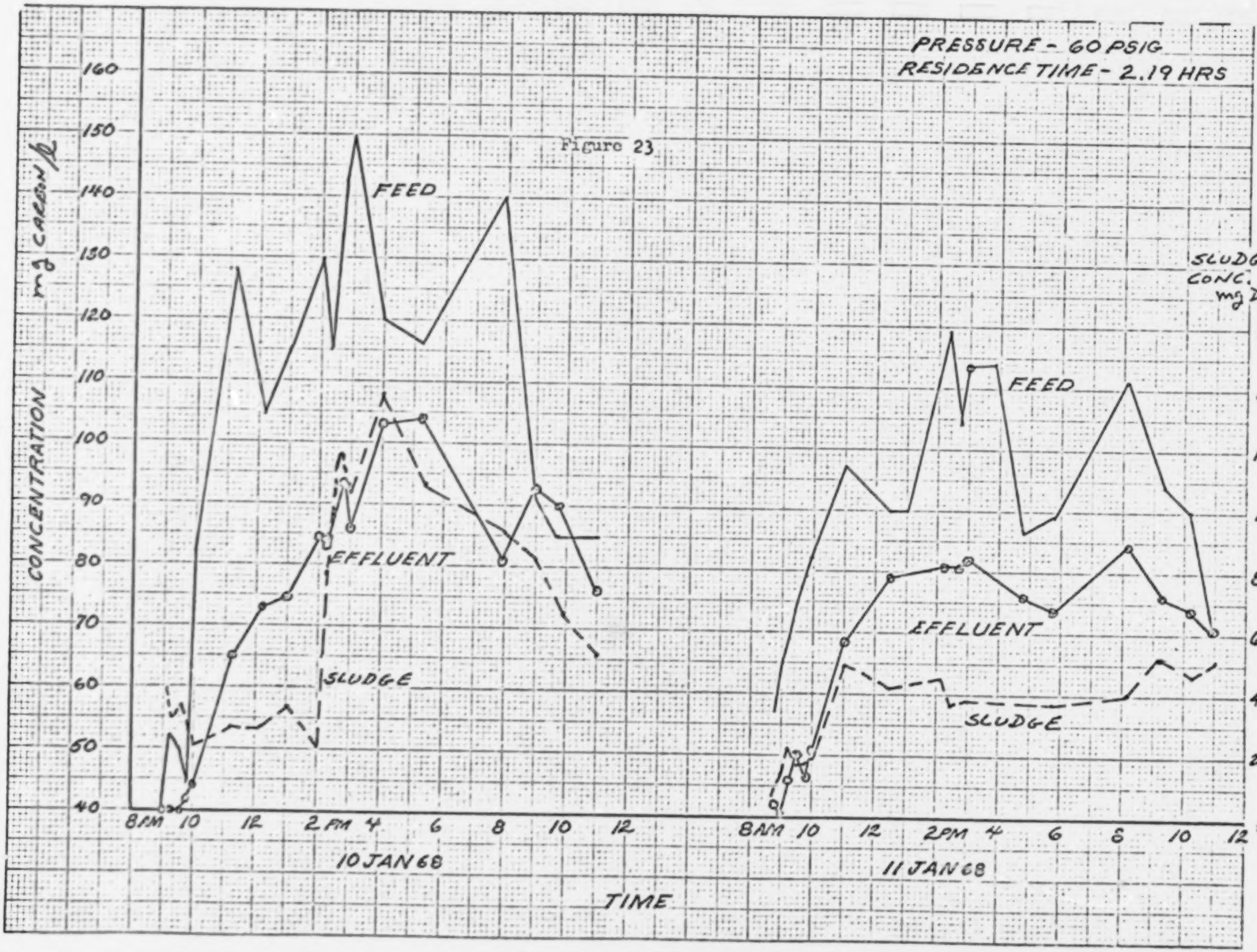

KEUFFEL & ESSER CO.
PRESSURE - 60 PSIG
RESIDENCE TIME - 2.19 HRS
CONCENTRATION mg CARBON/l
160
150
140
130
120
110
100
90
80
70
60
50
40
FEED
EFFLUENT
SLUDGE
FEED
EFFLUENT
SLUDGE
SLUDGE CONC. mg DRY/l
160
140
120
100
80
60
40
20
0
8AM
10
12
2PM
4
6
8
10
12
10 JAN 68
8AM
10
12
2PM
4
6
8
10
12
11 JAN 68
TIME

Figure 23

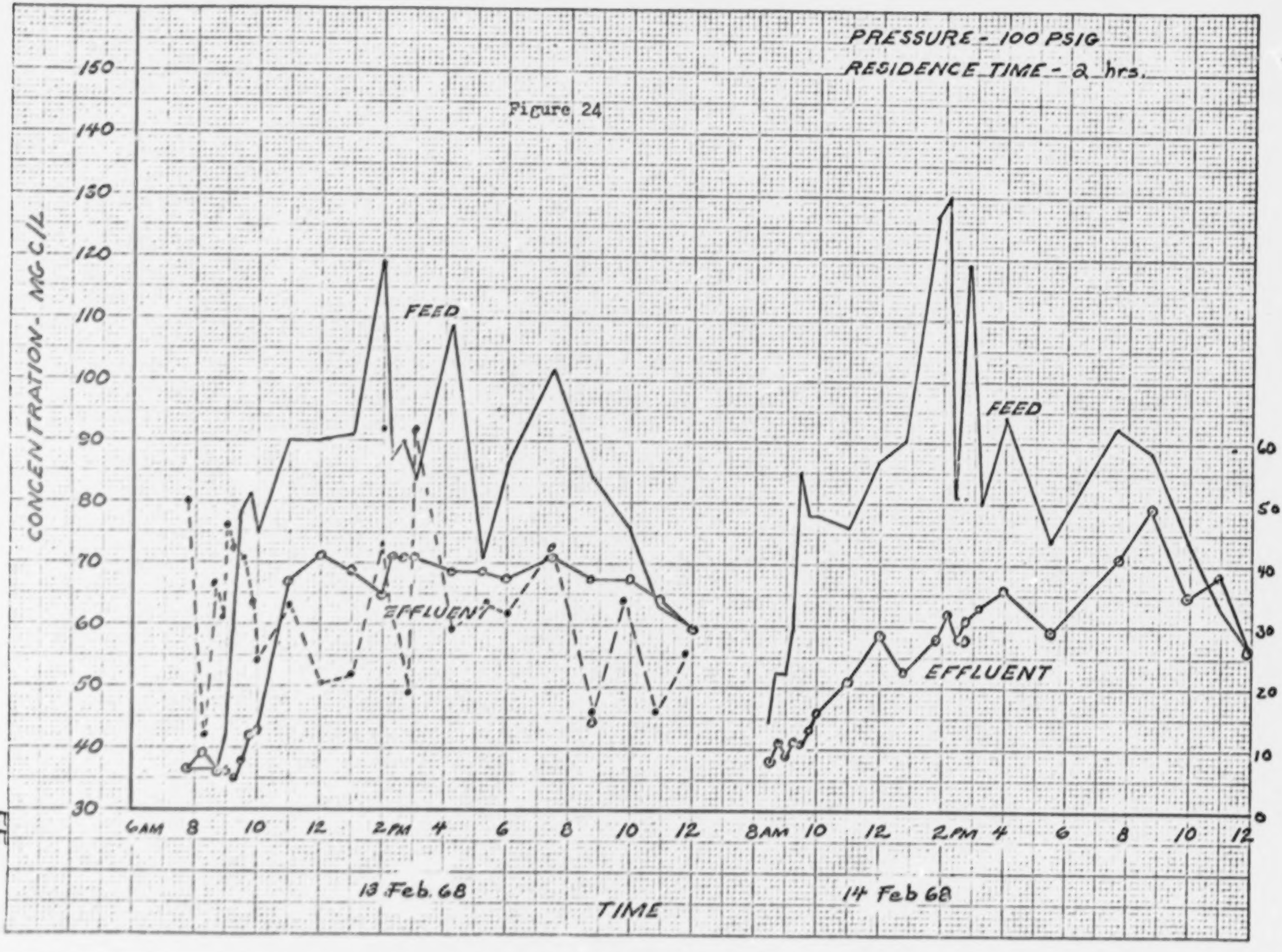


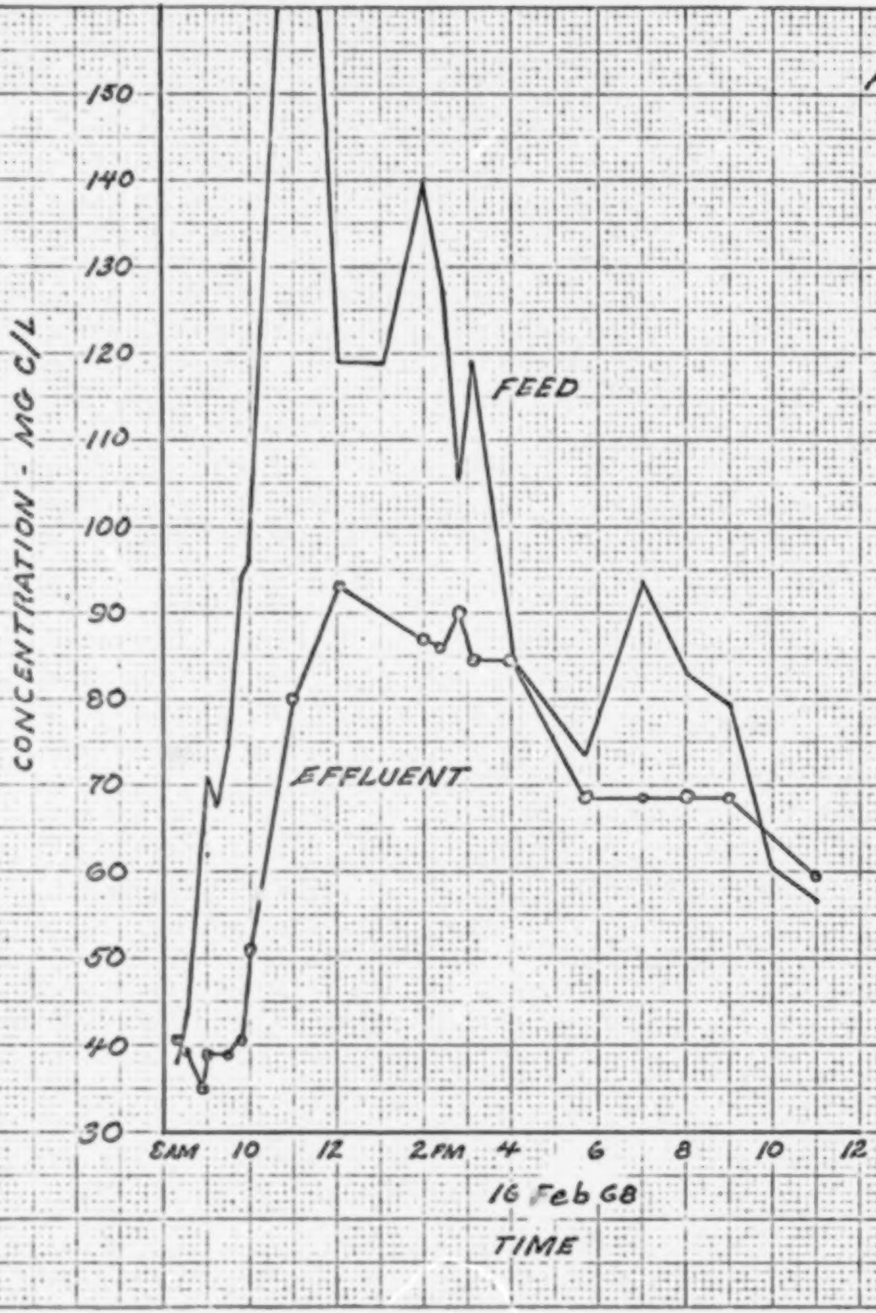
Figure 24

PRESSURE - 100 PSIG
RESIDENCE TIME - 2 hrs.
CONCENTRATION - MG C/L
150
140
130
120
110
100
90
80
70
60
50
40
30
60
50
40
30
20
10
0
FEED
EFFLUENT
FEED
EFFLUENT
6AM
8
10
12
2PM
4
6
8
10
12
8AM
10
12
2PM
4
6
8
10
12
13 Feb. 68
14 Feb 68
TIME

K&E 10 X 10 TO ½ INCH 46 0770
7½ X 10 INCHES
KEUFFEL & ESSER CO.

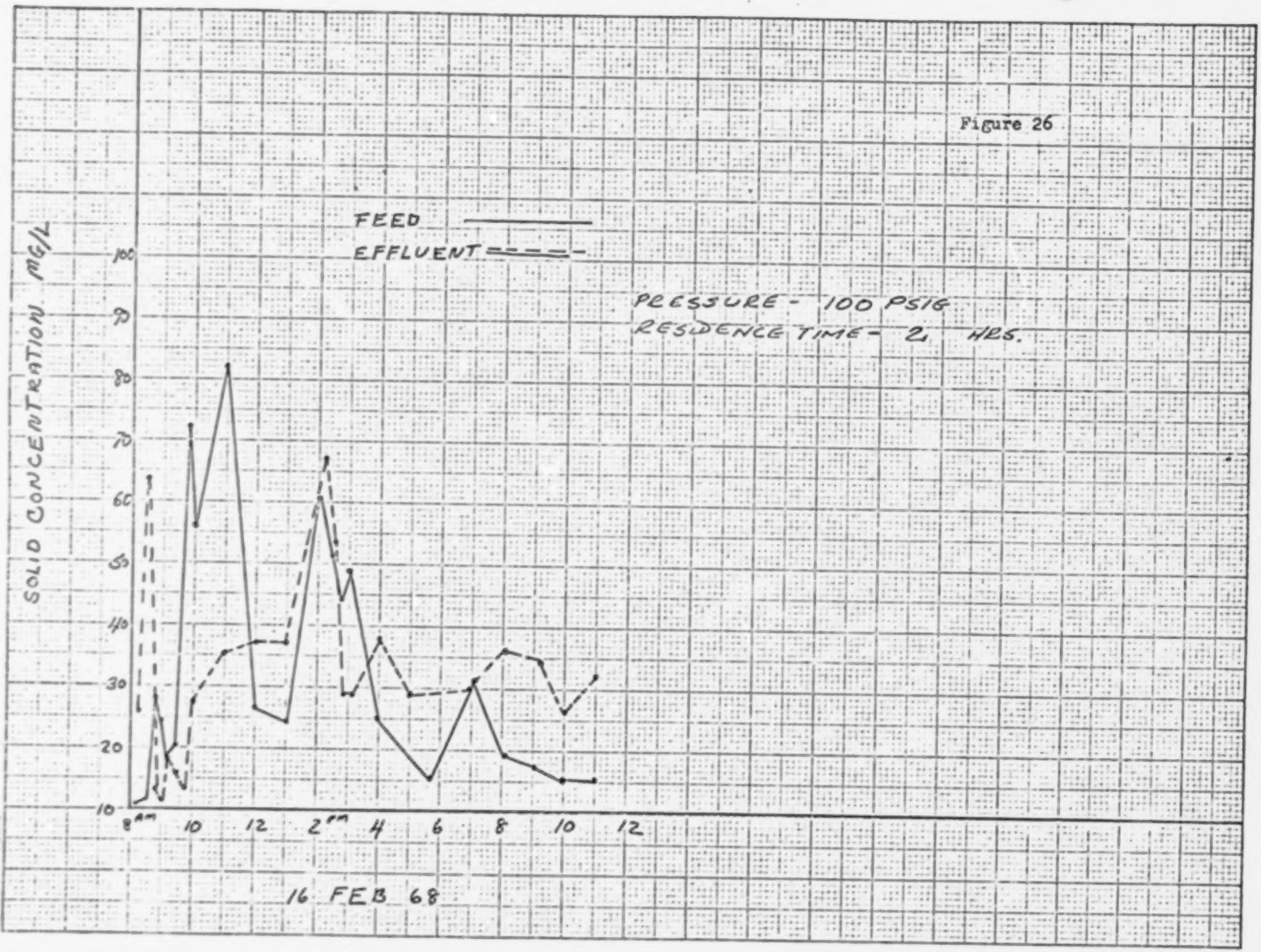
PRESSURE - 100 PSIG
RESIDENCE TIME - 2 hrs.

Figure 25



10 X 10 TO ½ INCH 46 1470
KEUFFEL & ESSER CO.

Figure 26



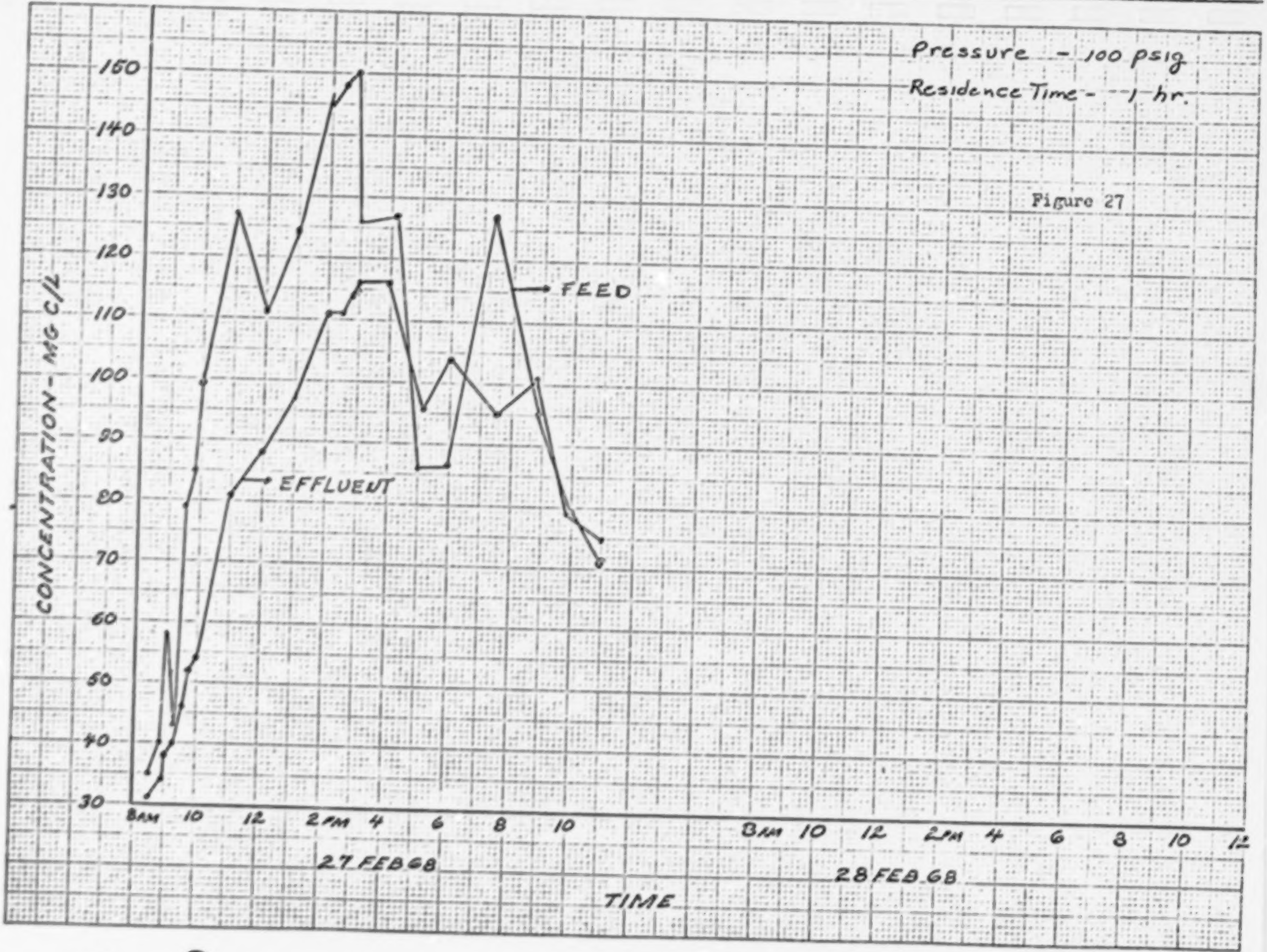
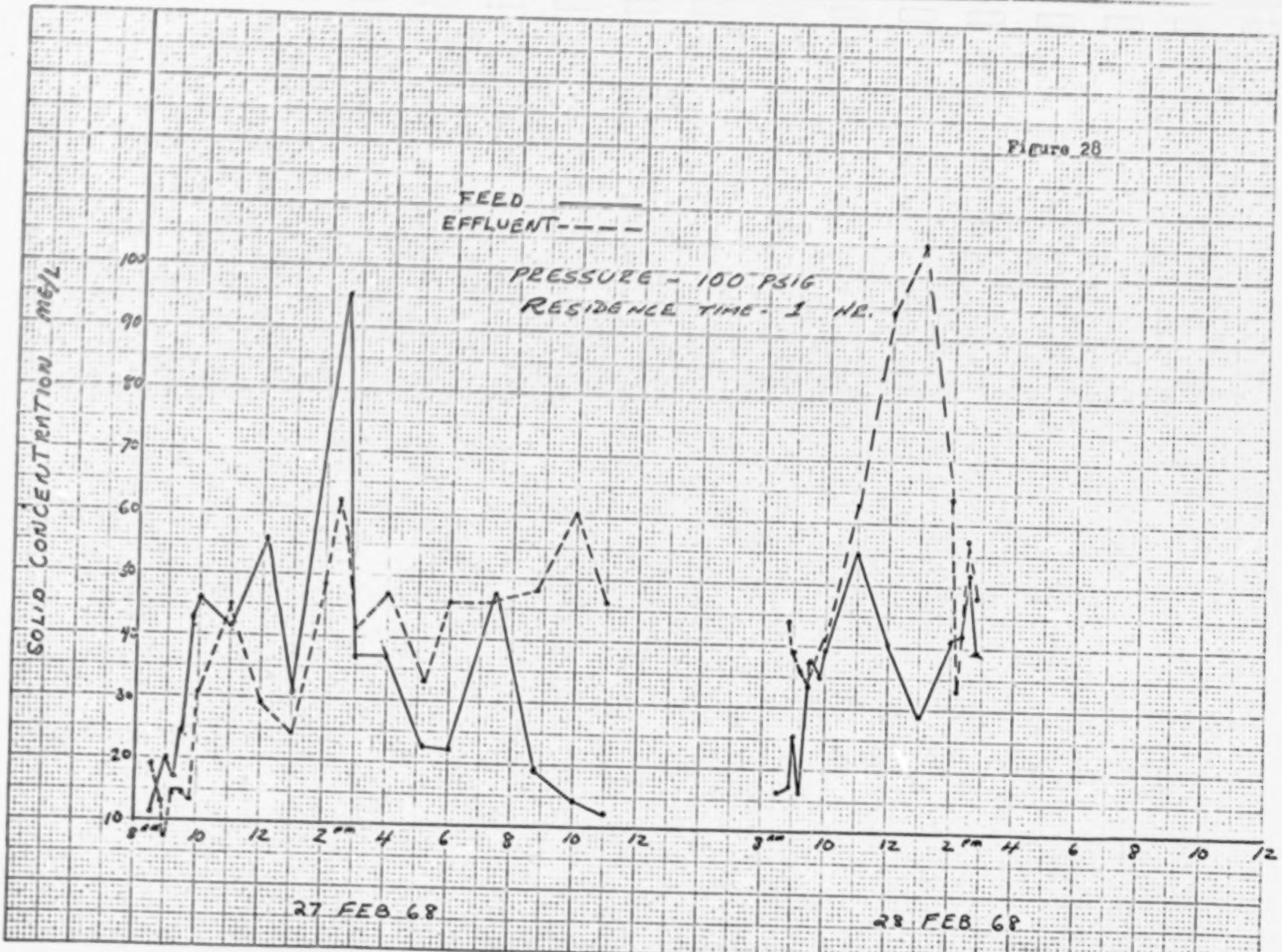

Pressure - 100 psig
Residence Time - 1 hr.
CONCENTRATION - MG C/L
150
140
130
120
110
100
90
80
70
60
50
40
30
FEED
EFFLUENT
8AM
10
12
2PM
4
6
8
10
8AM
10
12
2PM
4
6
8
10
12
27 FEB 68
28 FEB 68
TIME

Figure 27

Figure 28



K&E 10 X 10 TO ½ INCH 46 1470
7½ X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

K&E 10 X 10 TO 1/2 INCH 46 1
7 1/2 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

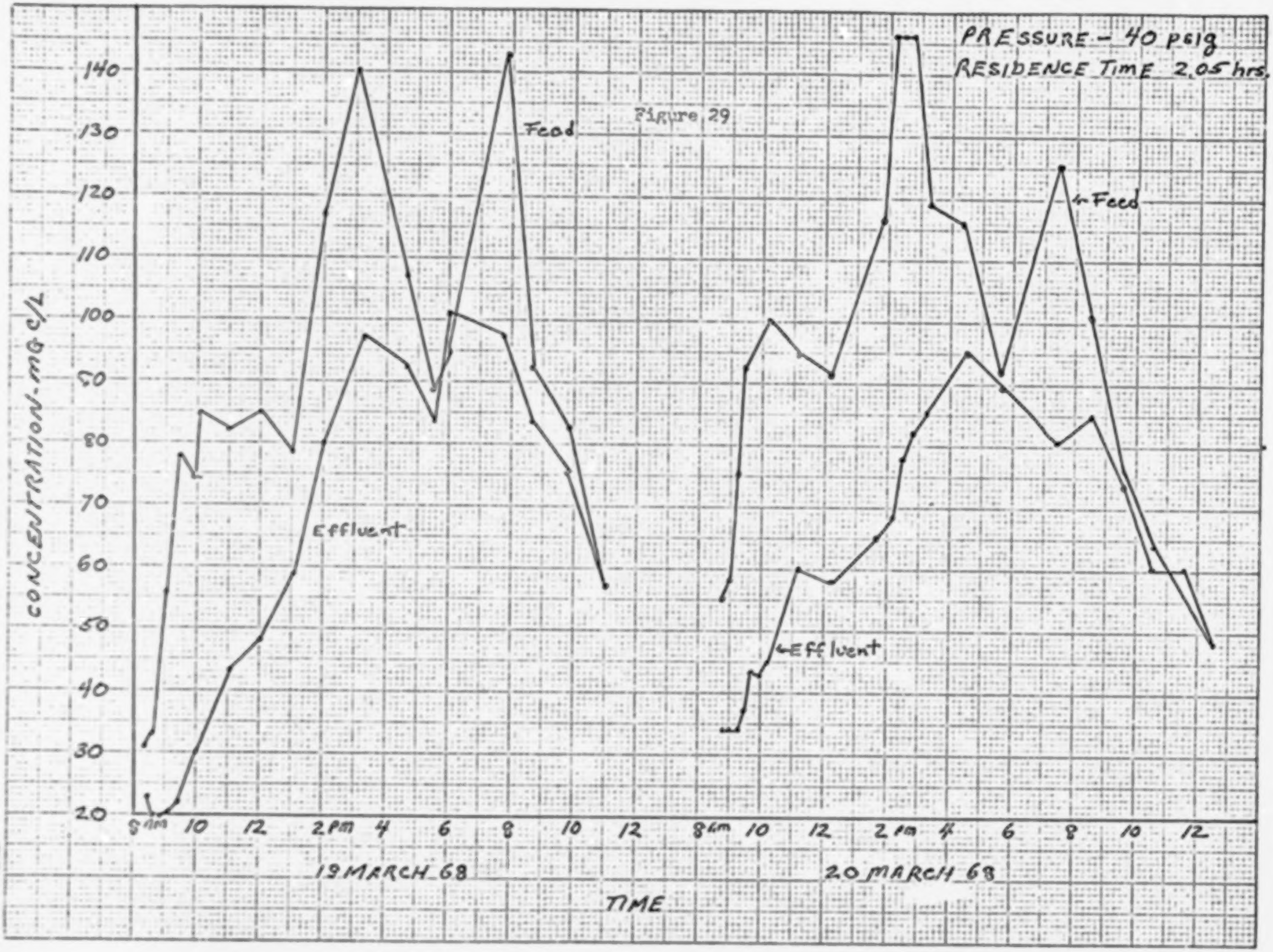
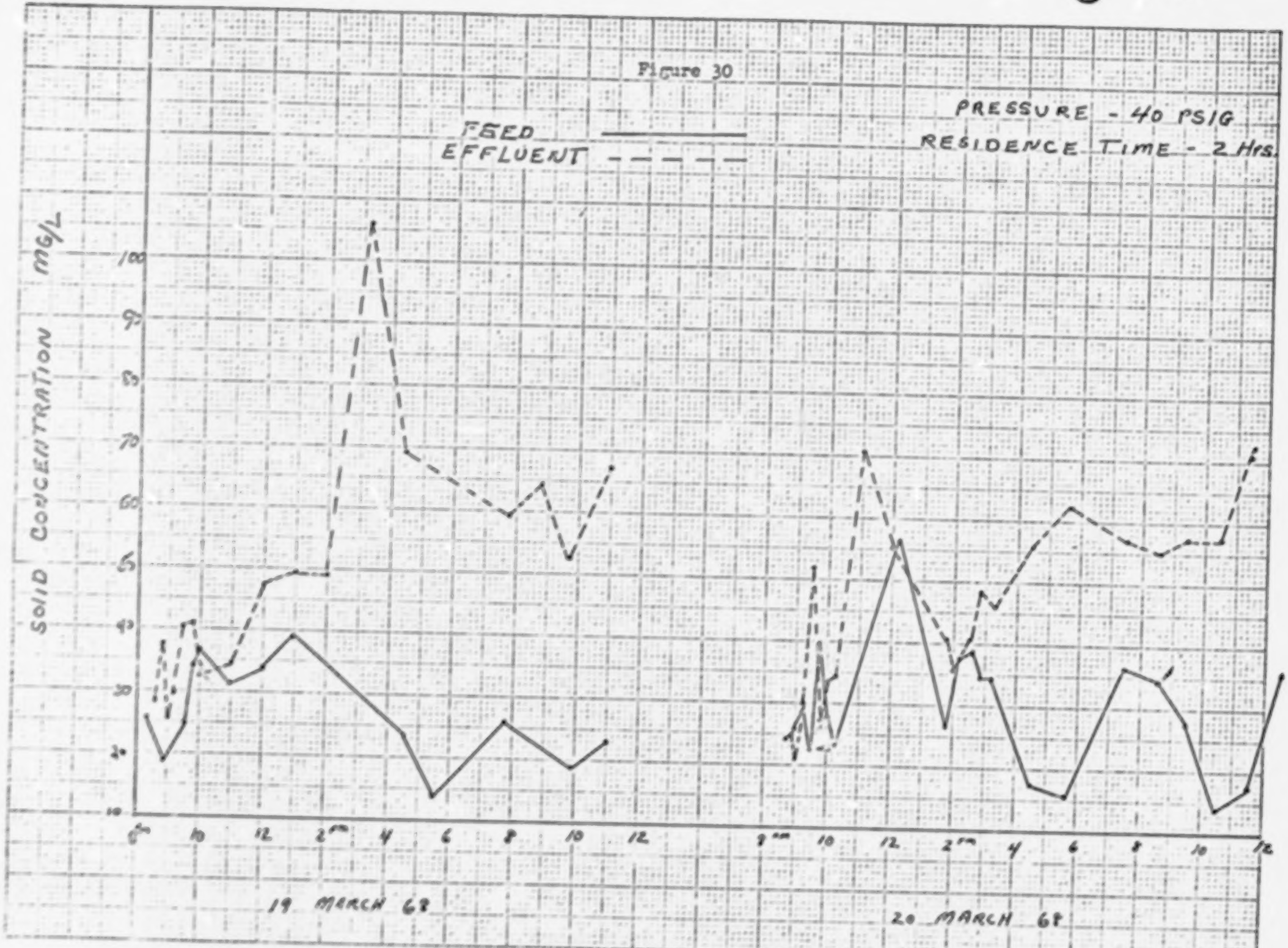


Figure 29

KEUFFEL & ESSER CO.

Figure 30



KEUFFEL & ESSER CO.

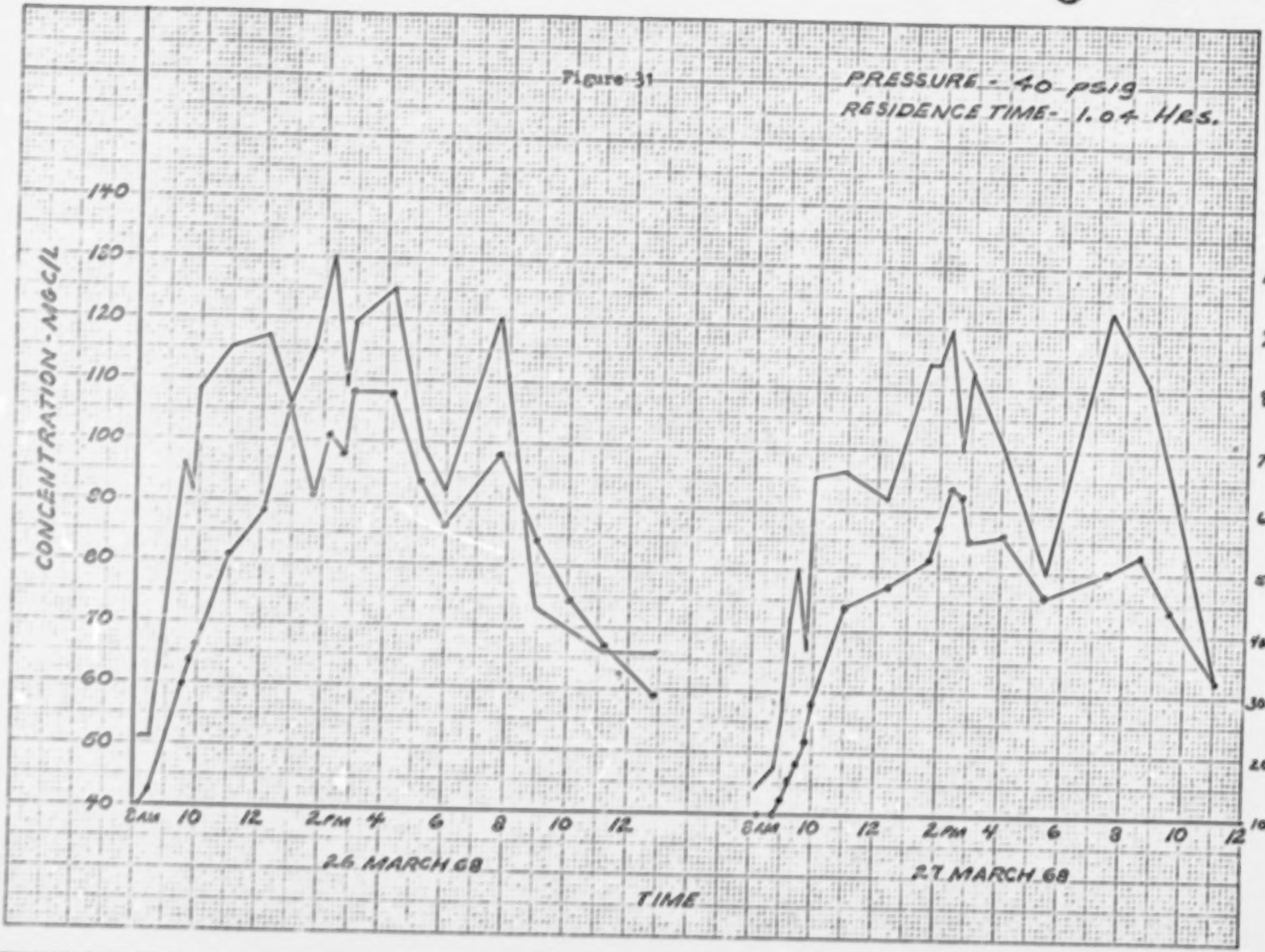
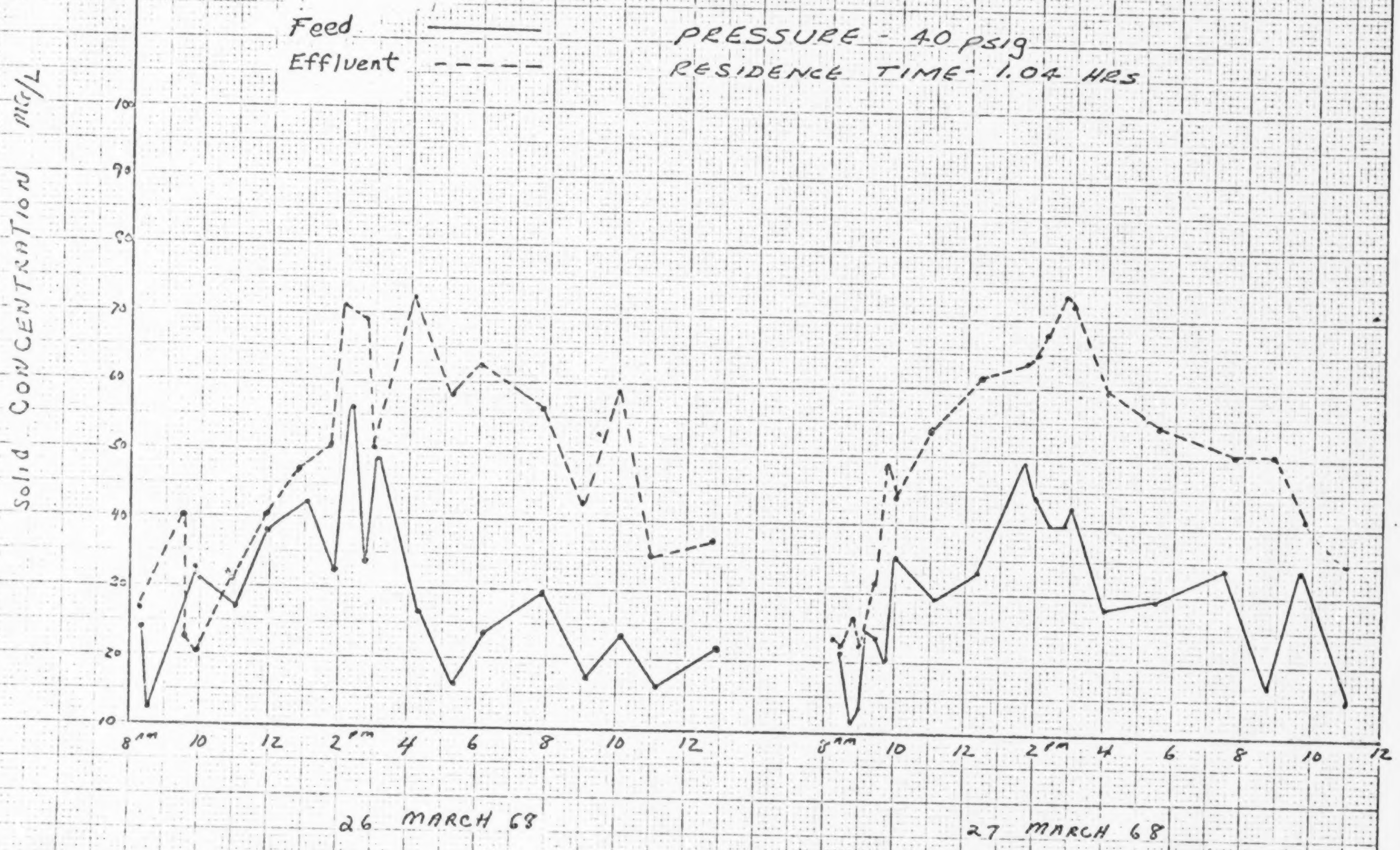


Figure 31

K&E 10 X 10 TO 1/2 INCH 46 0
7 1/2 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure 32



KEUFFEL & ESSER CO.

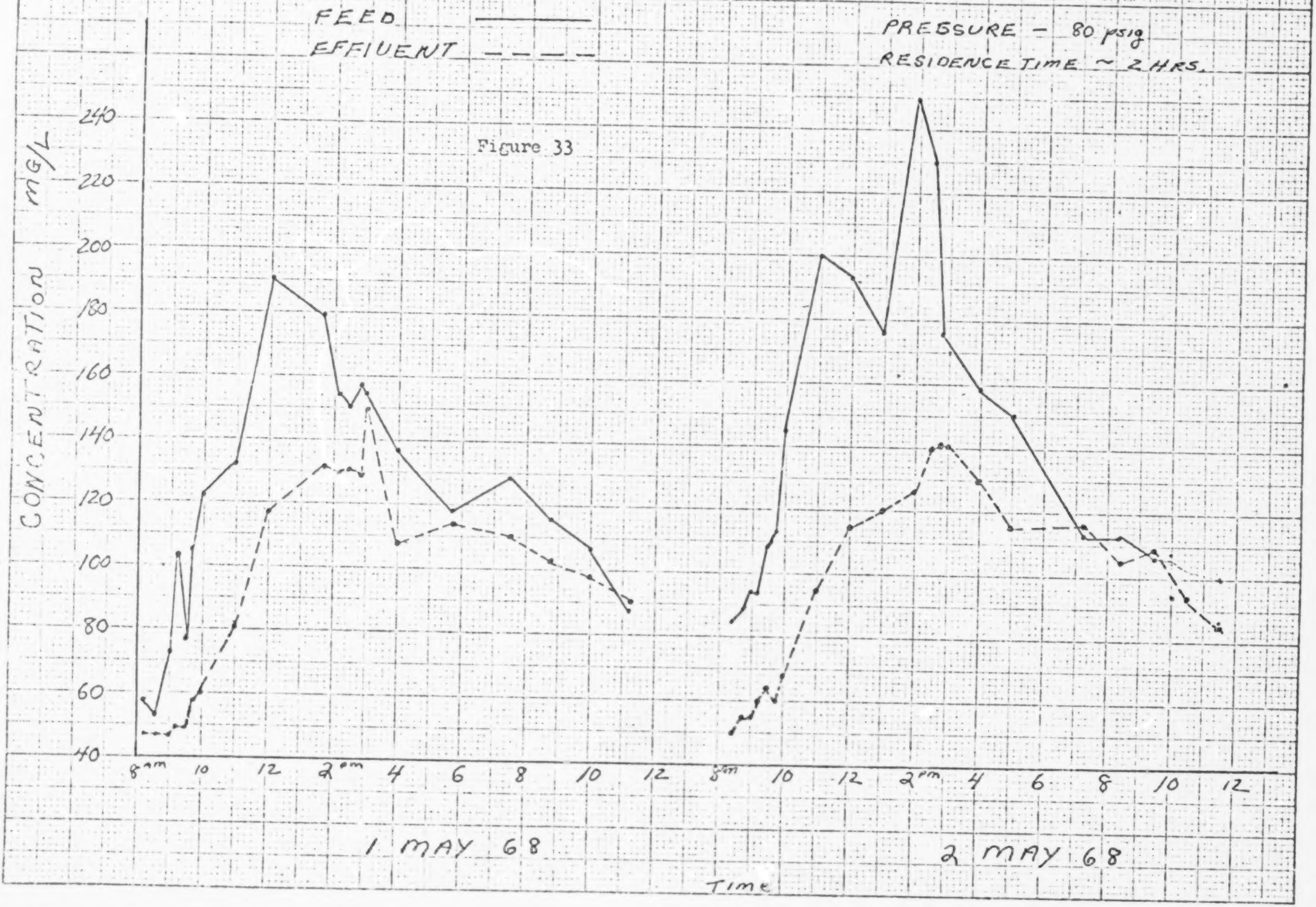
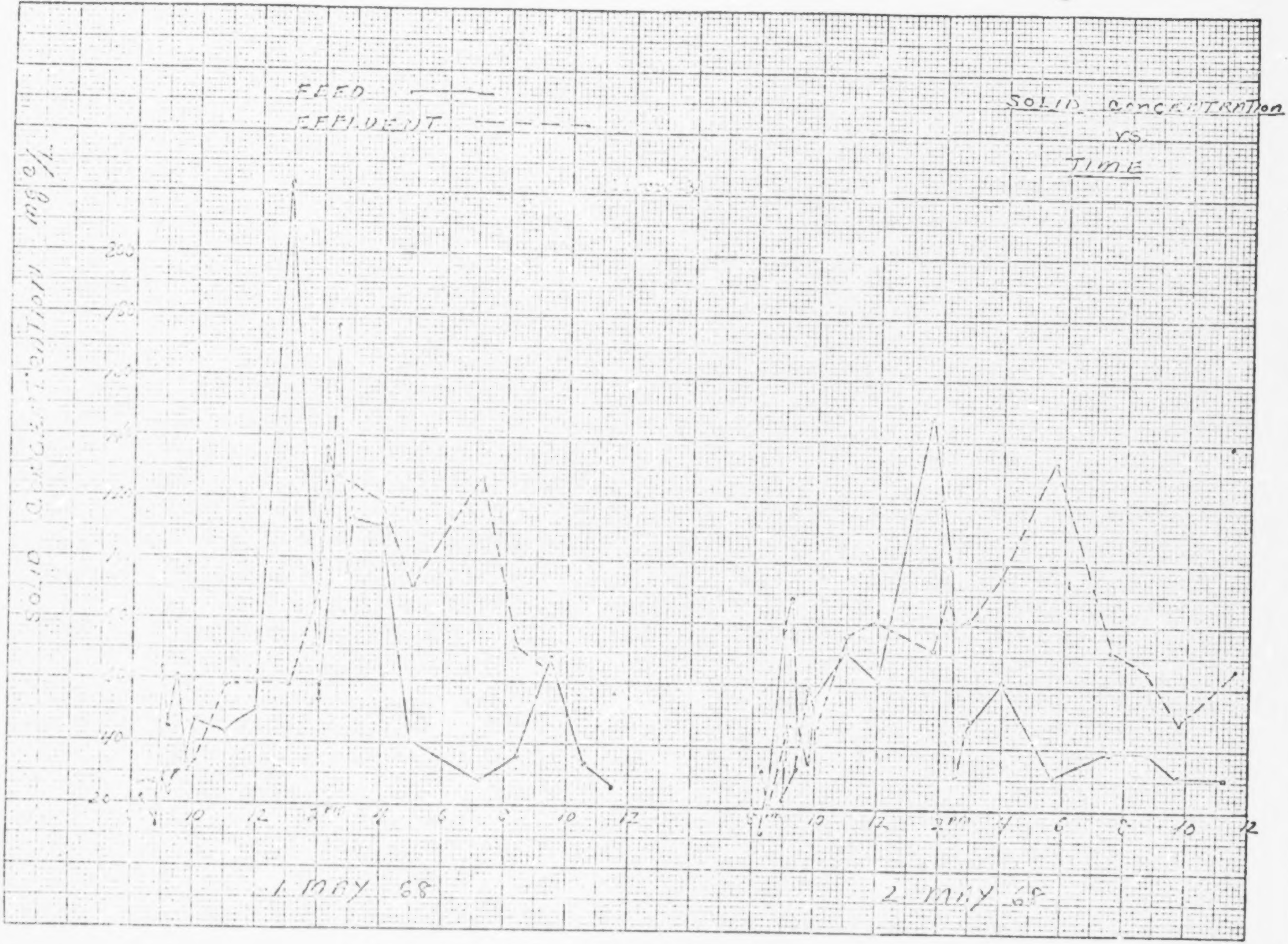


Figure 33

10 X 10 TO 1/2 INCH 46 1473
KEUFFEL & ESSER CO.



KEUFFEL & ESSER CO.

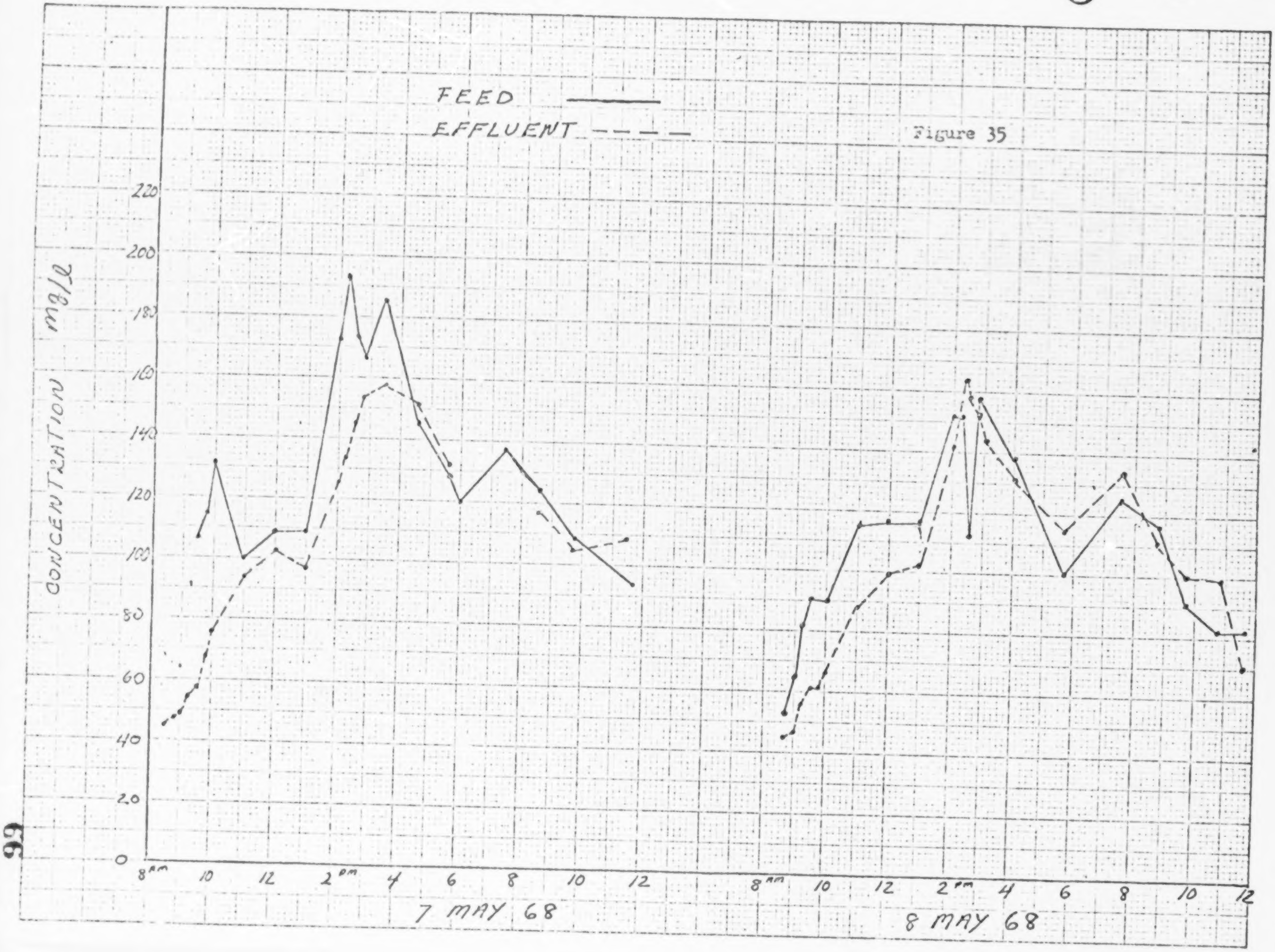
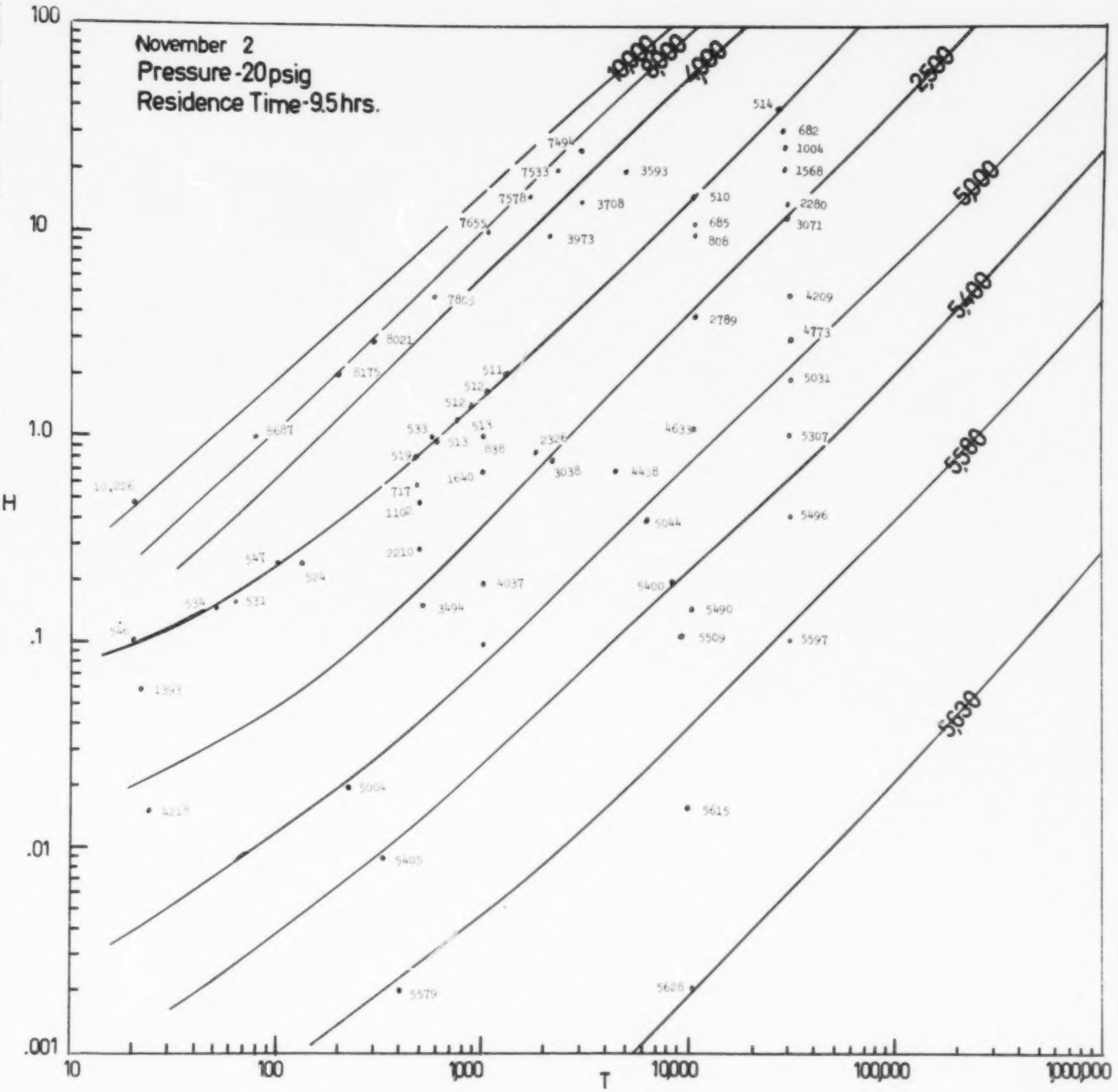
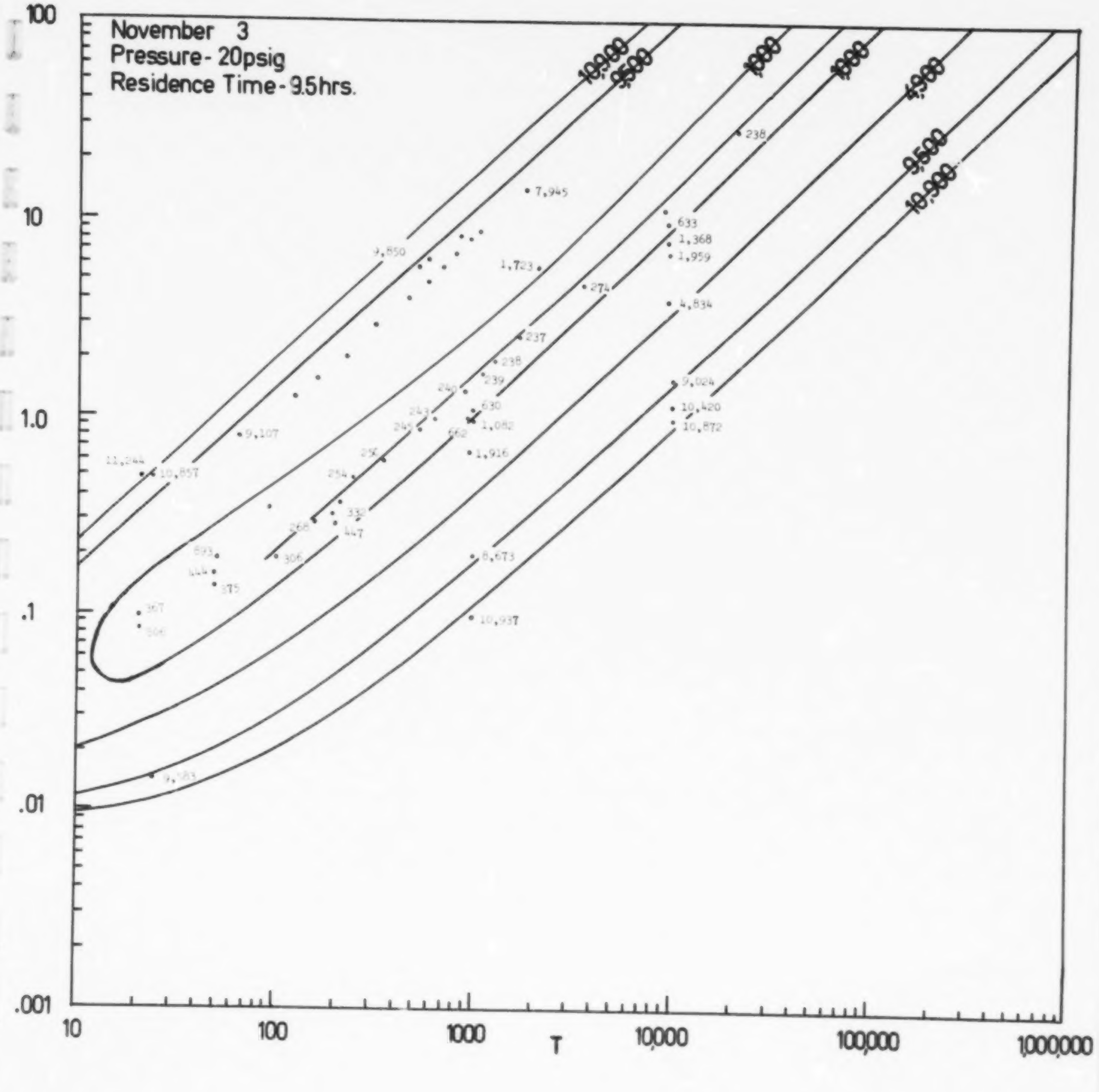
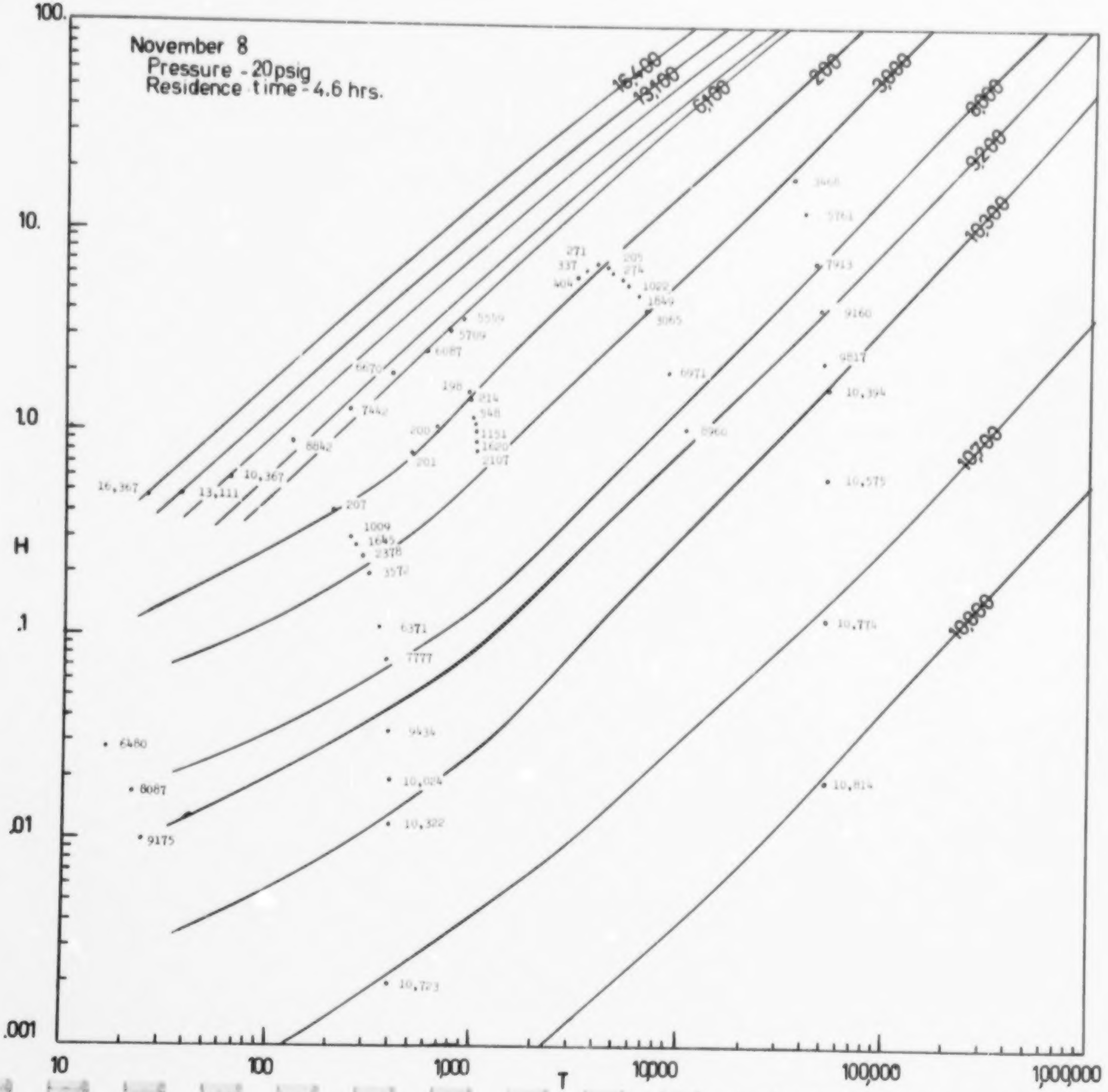
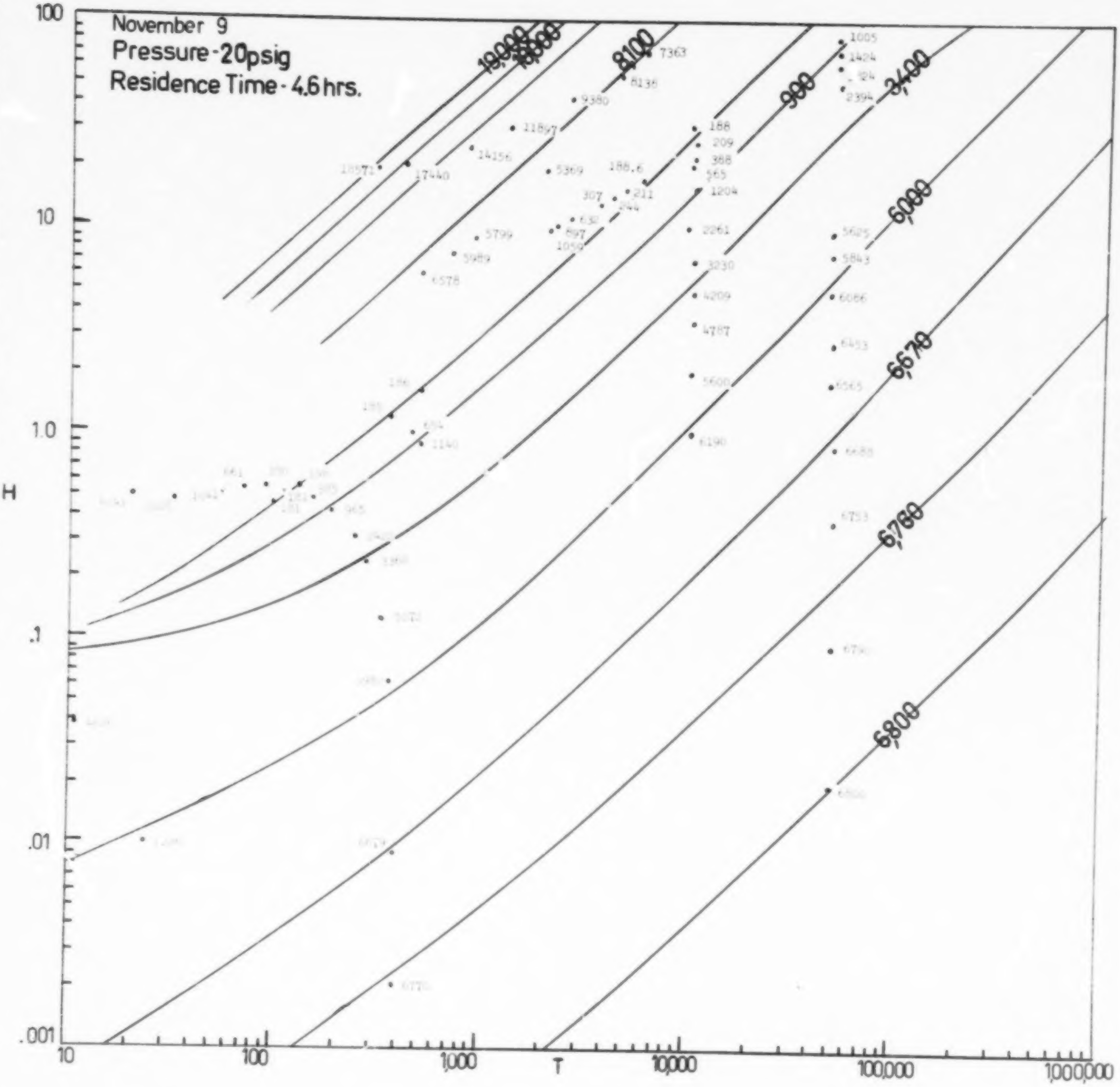


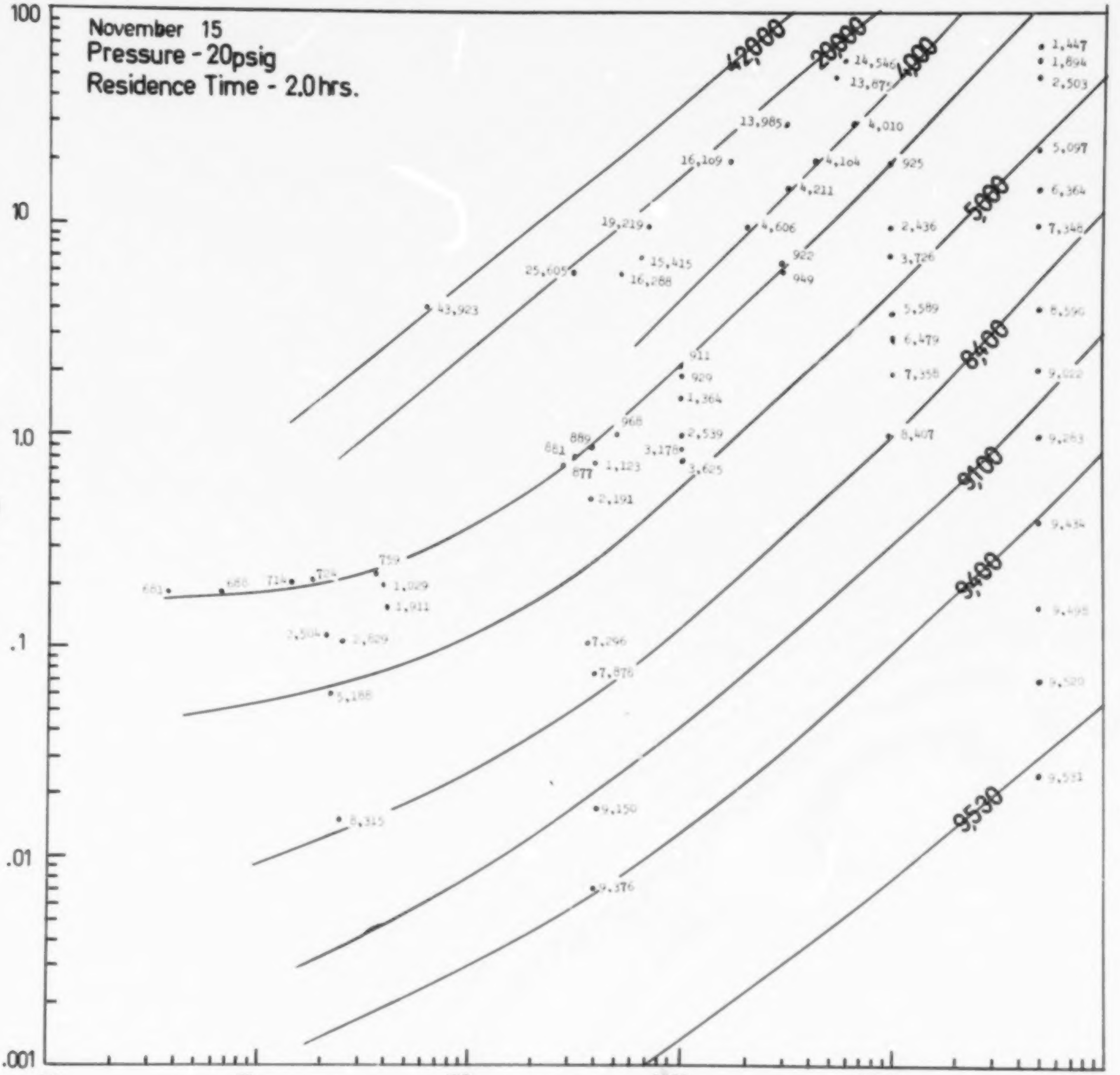
Figure 35


November 2
Pressure-20 psig
Residence Time-9.5 hrs.
100
10
1.0
.1
.01
.001
H
10
100
1,000
10,000
100,000
1,000,000
T
10,000
8,000
4,000
2,500
5,000
5,400
5,580
5,630
514
682
1004
1568
7494
7533
3593
7578
3708
510
2280
685
7655
3973
808
3071
7803
4209
2789
8021
4773
8175
511
512
512
5031
513
533
513
838
4633
5307
5687
2326
519
3038
1640
4438
10,226
717
1108
5496
5044
2210
547
524
4037
5400
534
531
3494
5490
546
5509
5597
1393
5004
4218
5615
5405
5579
5628

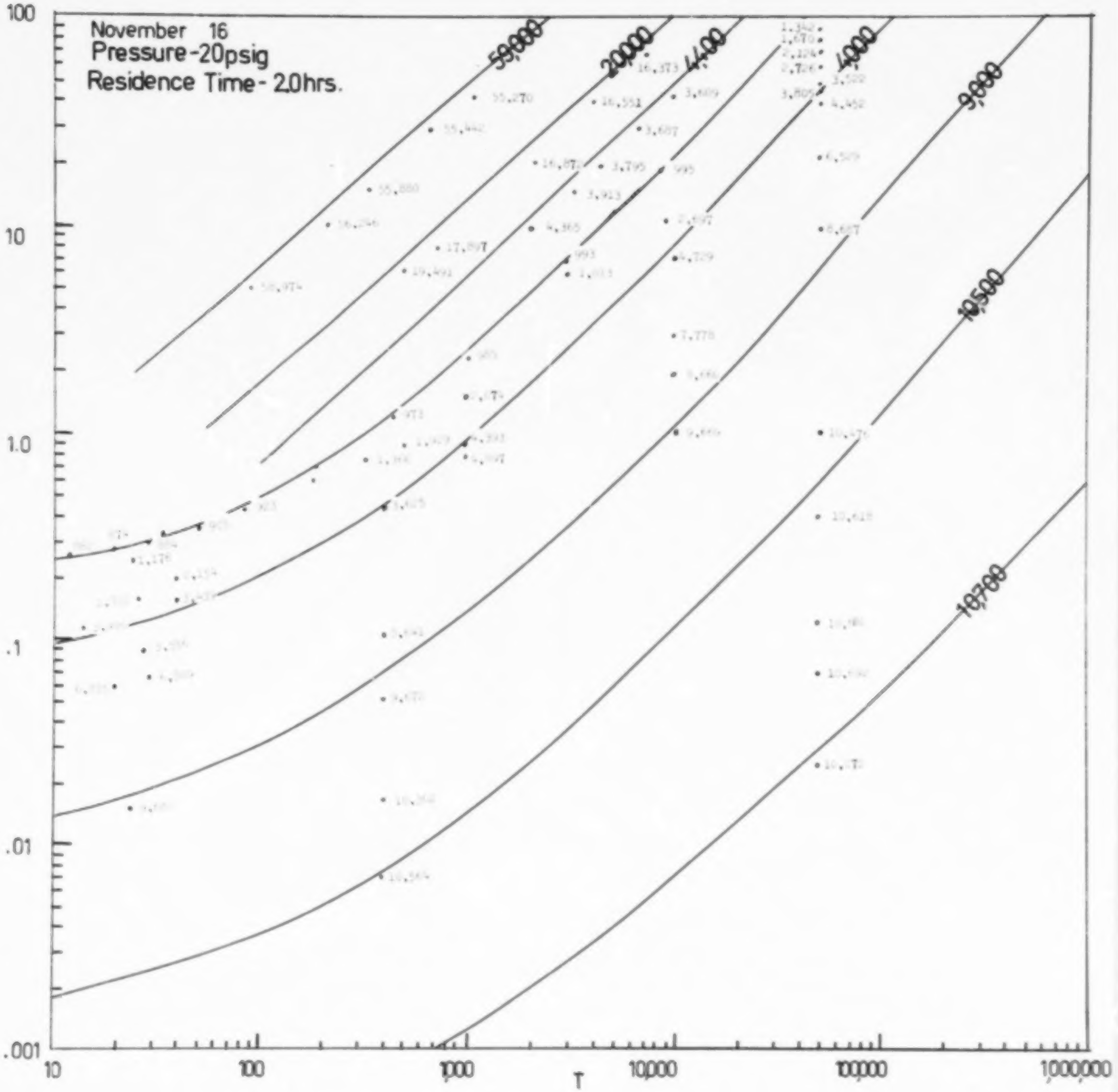

November 3
Pressure - 20psig
Residence Time - 9.5hrs.
10,000
9,500
1,000
1,000
4,900
9,500
10,000
238
7,945
633
1,368
1,959
9,850
1,723
274
4,834
237
238
239
240
630
243
245
1,082
662
9,024
10,420
10,872
9,107
11,244
10,857
256
254
1,916
332
268
447
306
693
444
375
8,673
367
306
10,937
9,183
100
10
1.0
.1
.01
.001
10
100
1000
T
10,000
100,000
1,000,000

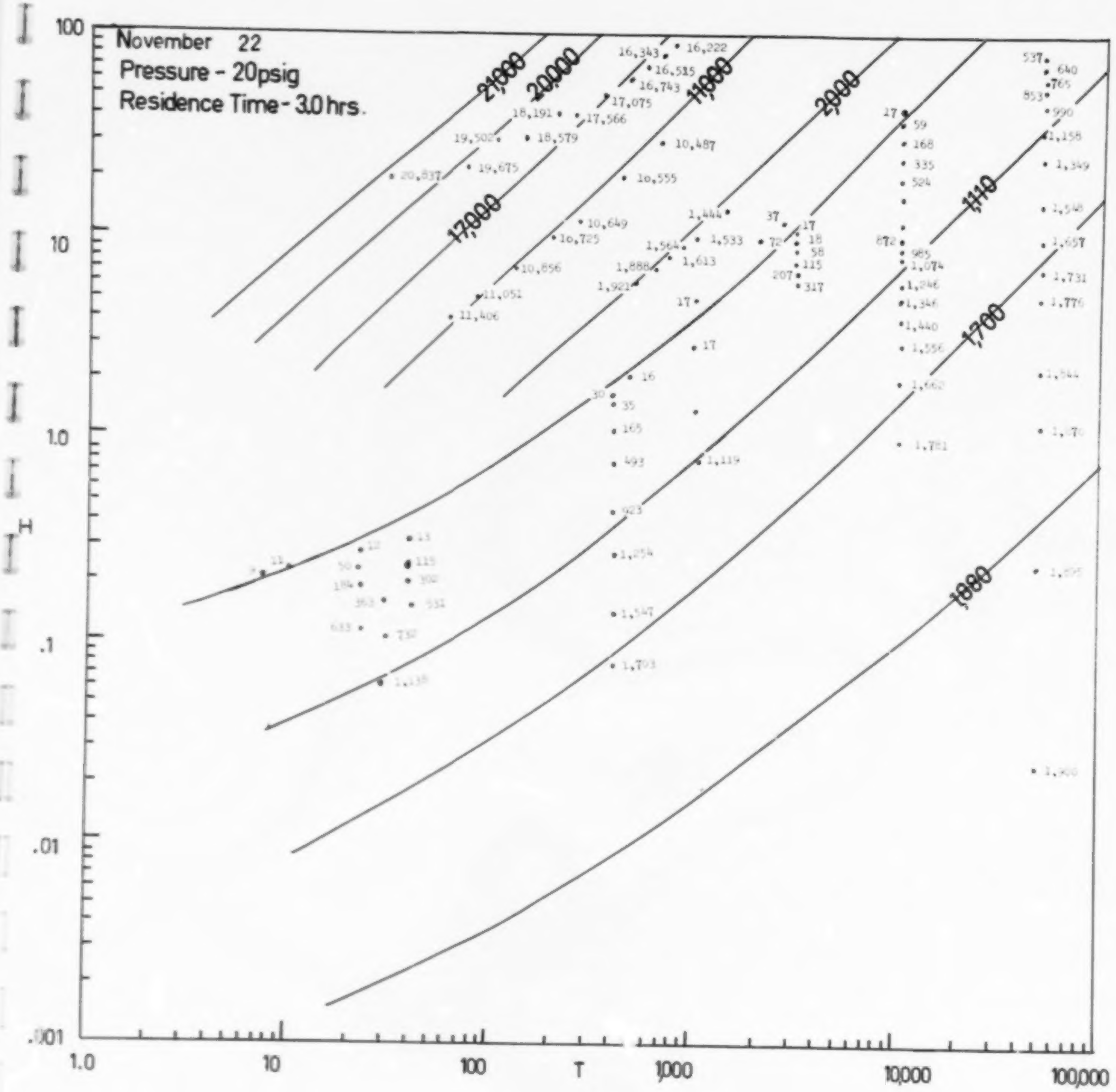

November 8
Pressure - 20psig
Residence time - 4.6 hrs.
16,400
13,100
6,100
200
3,800
8,000
9,200
10,300
10,700
10,800
16,367
13,111
10,367
8842
7442
6670
6087
5709
5559
207
1009
1645
2378
3572
200
201
198
214
948
1151
1620
2107
271
337
404
205
274
1022
1649
3065
6971
8966
3468
5761
7913
9160
9817
10,394
10,575
10,774
10,814
6371
7777
9434
10,024
10,322
10,723
6480
8087
9175
H
100.
10.
1.0
.1
.01
.001
T
10
100
1000
10000
100,000
1,000,000

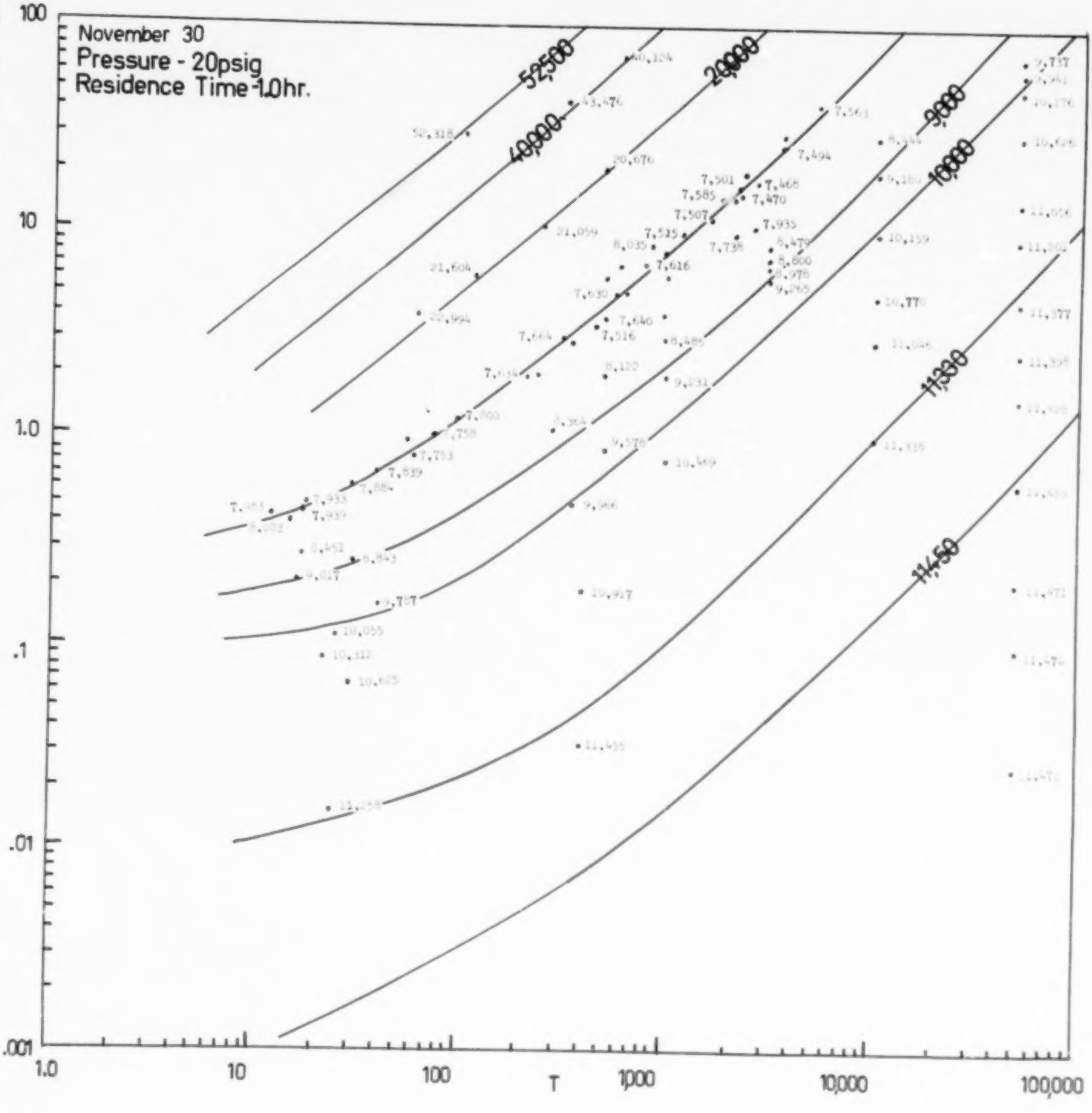

November 9
Pressure - 20psig
Residence Time - 4.6 hrs.
19,000
8100
900
3400
6000
6670
6760
6800
7363
8136
9380
11897
14156
18571
17440
5369
188.6
307
211
244
632
897
1059
5799
5989
6578
188
209
388
565
1204
2261
3230
4209
4787
5600
6190
1005
1424
2394
5625
5843
6086
6453
6565
6688
6753
6790
6800
186
195
694
1140
661
965
1300
3072
6679
6770
H
T
100
10
1.0
.1
.01
.001
10
100
1,000
10,000
100,000
1,000,000

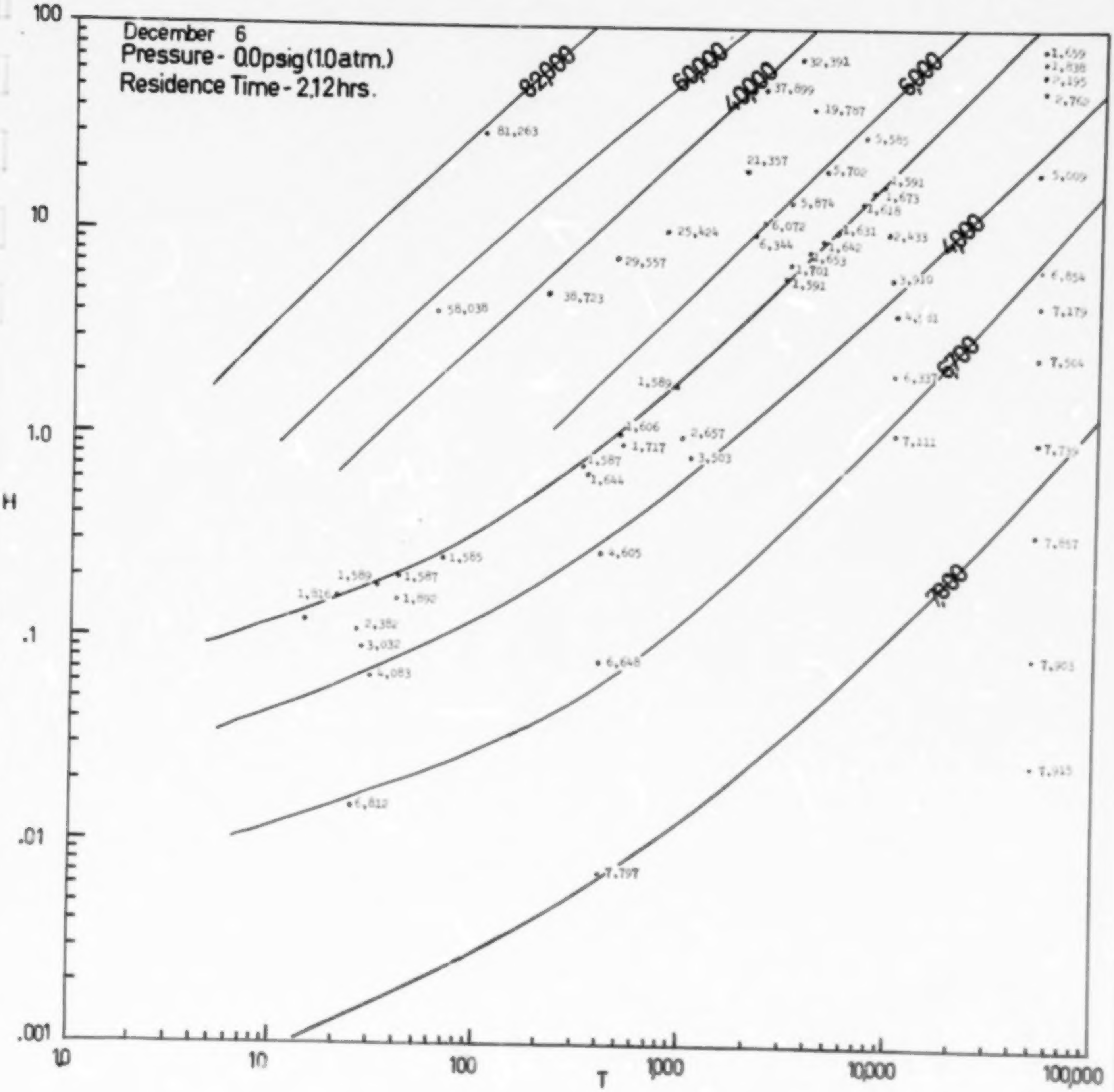


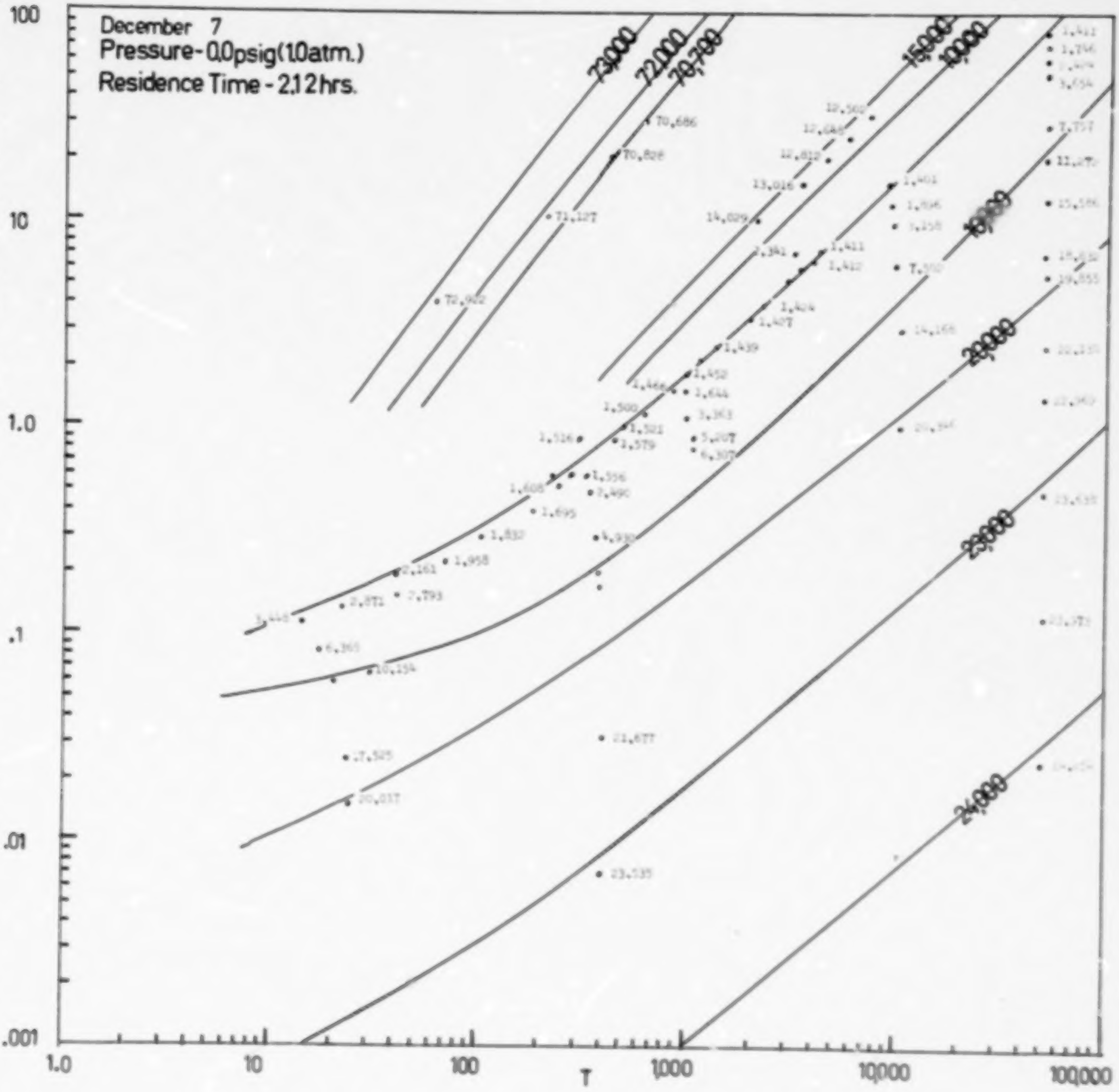
November 15
Pressure - 20psig
Residence Time - 2.0 hrs.

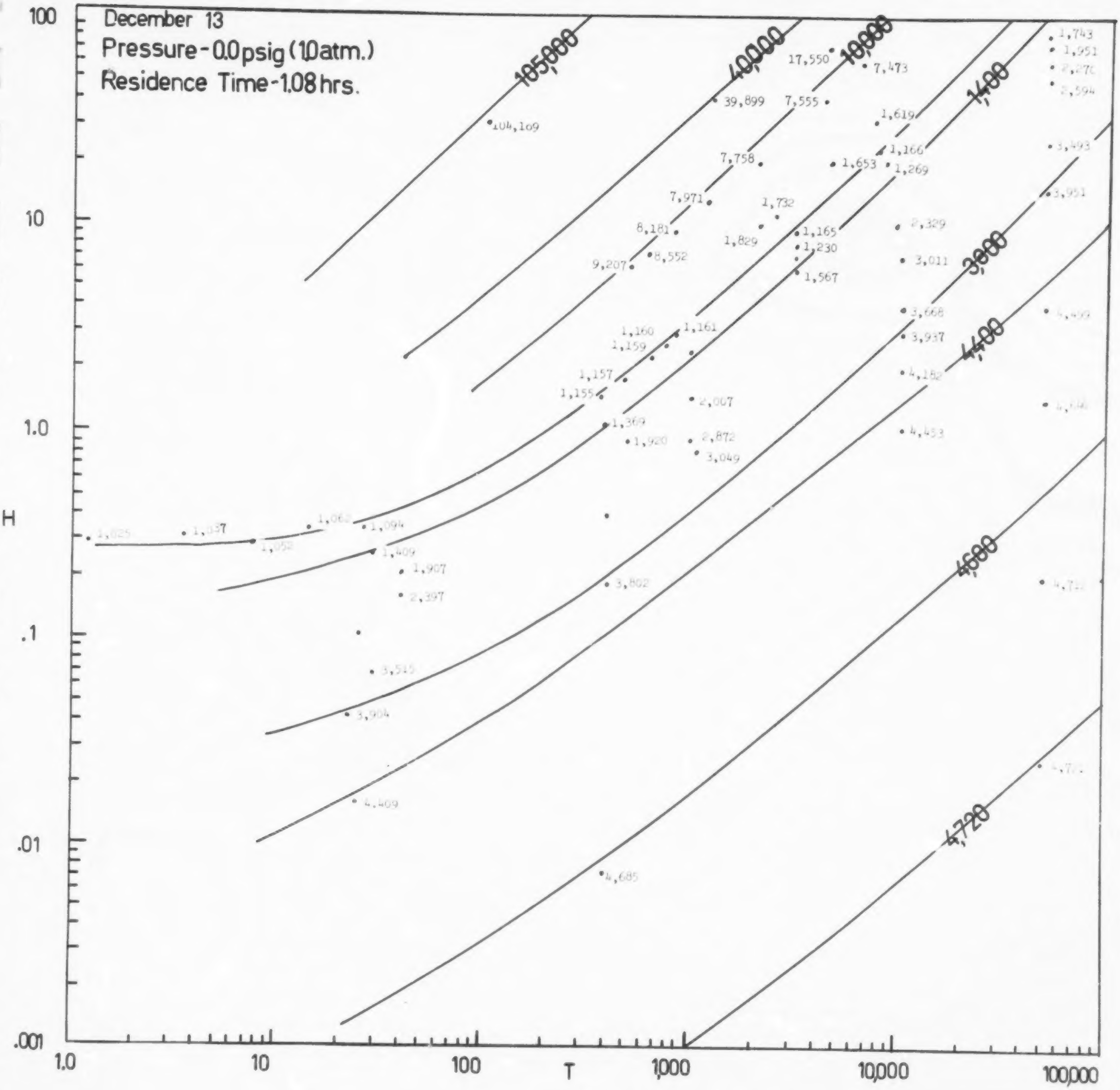

November 16
Pressure-20psig
Residence Time-2.0hrs.
59,000
20000
4400
4000
9,890
10,500
10,700
H
100
10
1.0
.1
.01
.001
T
10
100
1000
10,000
100,000
1,000,000

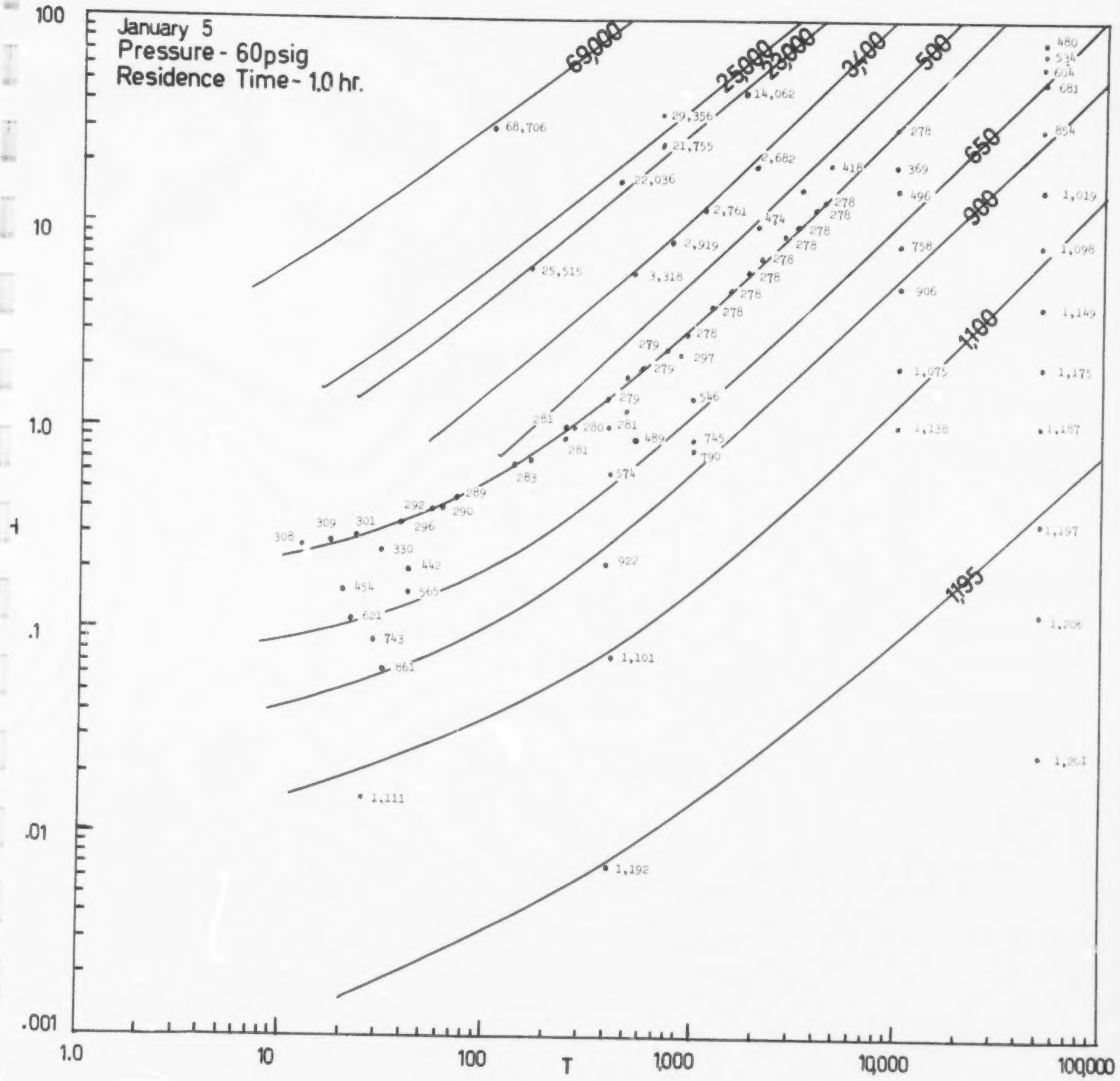

November 22
Pressure - 20psig
Residence Time - 3.0 hrs.
21,000
20,000
17,000
11,000
2,000
1,110
1,700
1,880
100
10
1.0
.1
.01
.001
H
1.0
10
100
T
1,000
10,000
100,000

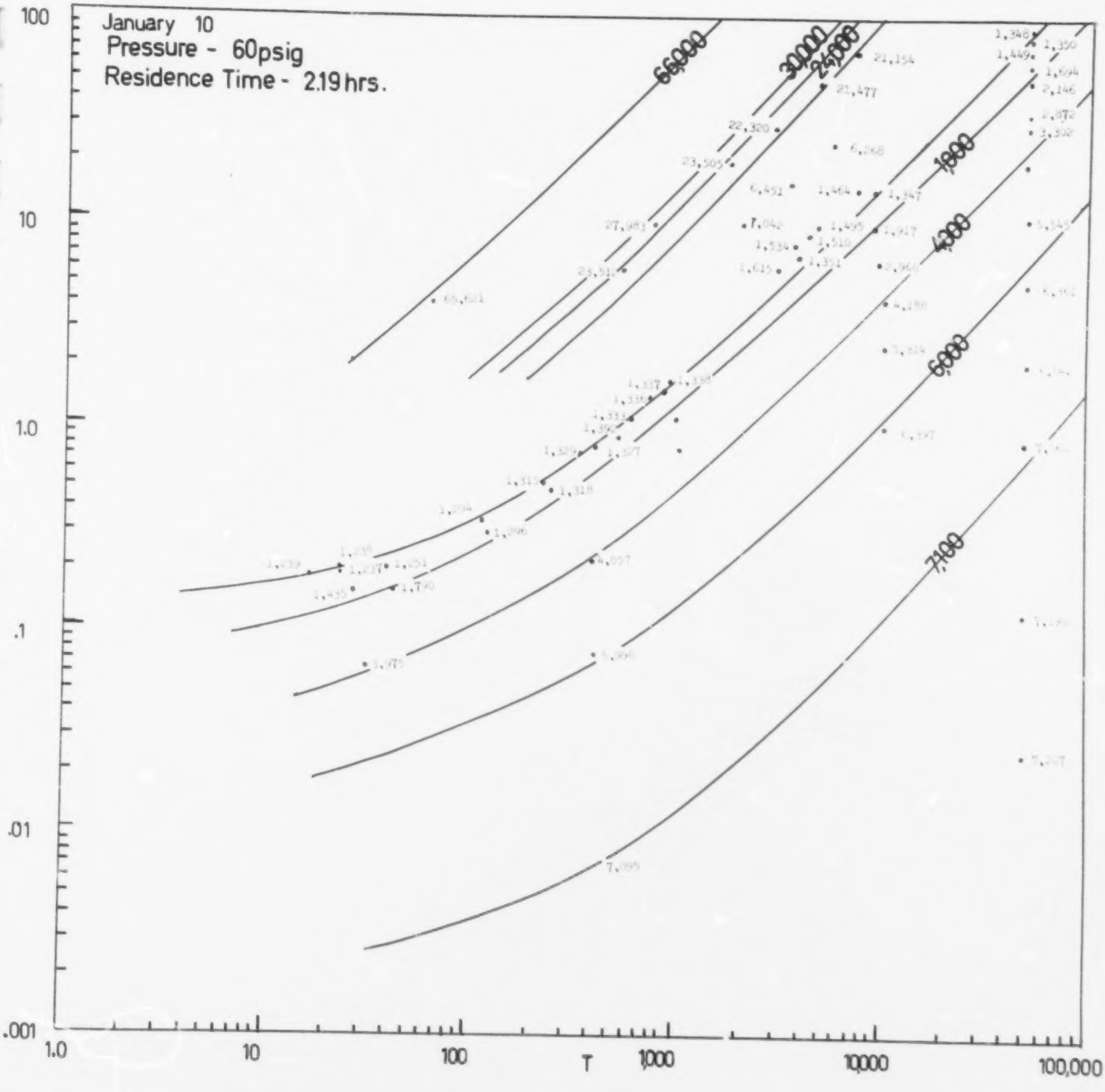

November 30
Pressure - 20psig
Residence Time-1.0hr.
52,500
40,000
20,000
9,000
10,000
11,330
11,450
52,318
40,104
43,476
20,676
21,059
21,604
22,994
7,563
7,494
7,501
7,468
7,585
7,470
7,507
7,935
7,515
8,035
7,738
8,479
8,600
7,616
8,978
9,265
7,630
7,640
7,664
7,516
8,485
7,634
8,122
9,031
7,800
7,758
8,364
7,753
9,578
7,839
10,469
7,884
7,983
7,933
7,939
8,003
9,966
8,451
8,843
9,017
9,787
10,917
10,055
10,312
10,625
11,455
8,344
9,180
10,159
10,770
11,046
11,335
9,737
9,941
10,176
10,626
11,056
11,202
11,377
11,398
11,471
11,474
100
10
1.0
.1
.01
.001
H
1.0
10
100
1,000
10,000
100,000
T

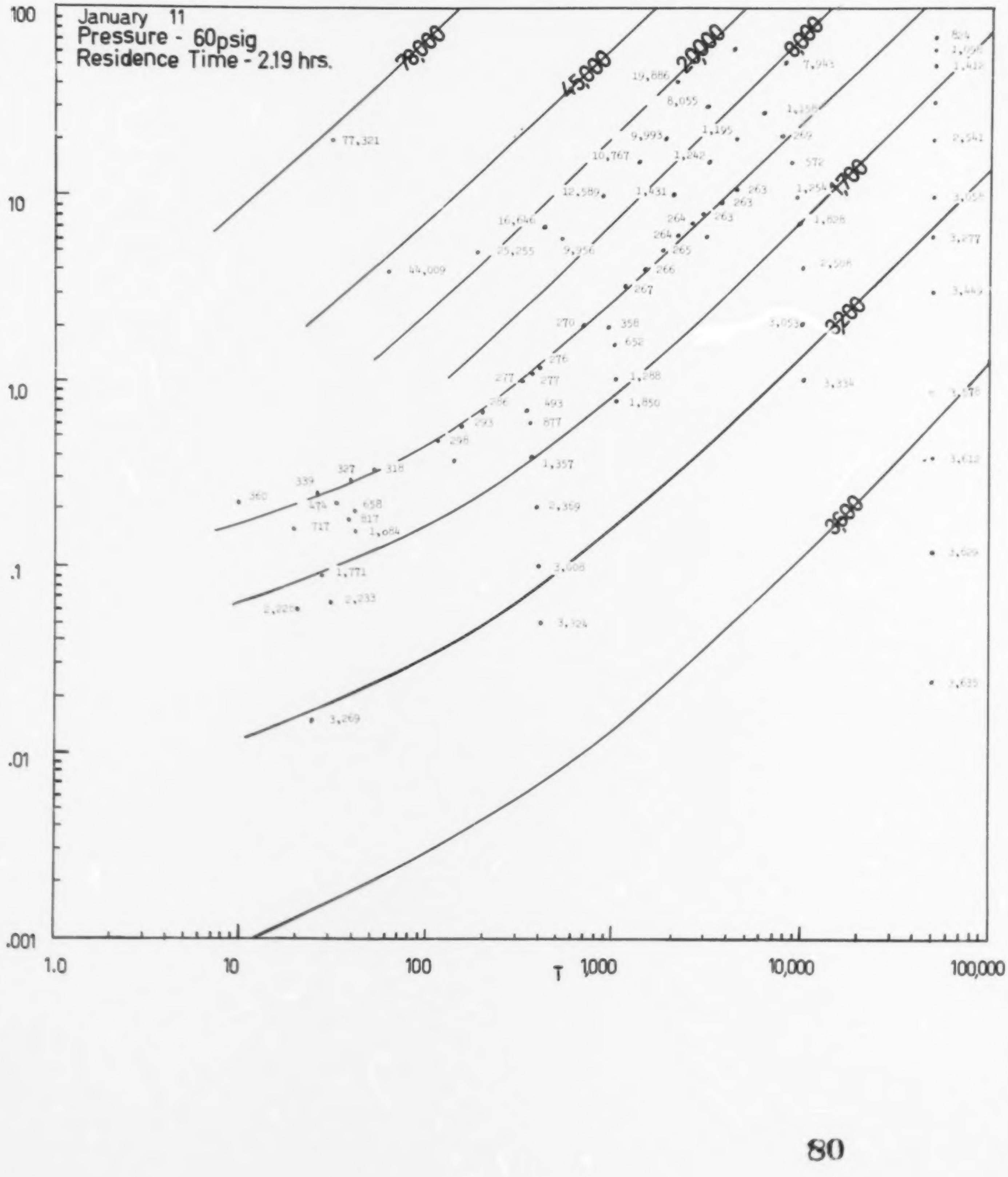

December 6
Pressure - 0.0psig (1.0atm.)
Residence Time - 2.12hrs.
82,000
60,000
40,000
6,000
4,000
6,700
7,800
81,263
58,038
38,723
29,557
25,424
21,357
32,391
37,899
19,787
5,585
5,702
5,874
6,072
6,344
1,591
1,673
1,618
1,631
1,642
2,653
1,701
1,591
2,433
3,910
6,337
7,111
1,659
1,838
2,195
2,762
5,009
6,854
7,179
7,504
7,739
7,857
7,903
7,915
1,589
1,606
1,717
1,587
1,644
2,657
3,503
1,585
1,589
1,587
1,816
1,890
2,382
3,032
4,083
4,605
6,648
6,812
7,797
100
10
1.0
.1
.01
.001
H
1.0
10
100
1000
10,000
100,000
T


December 7
Pressure - 0.0psig(1.0atm.)
Residence Time - 2.12 hrs.
73,000
72,000
70,700
15,000
10,000
18,000
20,000
23,000
24,000
70,686
70,828
71,127
72,902
12,502
12,646
12,812
13,016
14,029
2,341
1,411
1,412
1,424
1,407
1,439
1,452
1,466
1,644
1,500
3,363
1,521
1,516
1,579
5,207
6,307
1,556
1,608
2,490
1,695
1,832
4,930
2,161
1,958
2,871
7,793
3,446
6,365
10,154
7,525
20,037
21,677
23,135
1,401
1,896
3,158
7,550
14,166
20,346
1,411
1,786
3,654
7,757
11,272
15,586
18,832
19,855
22,235
22,960
23,638
100
10
1.0
.1
.01
.001
1.0
10
100
T
1,000
10,000
100,000

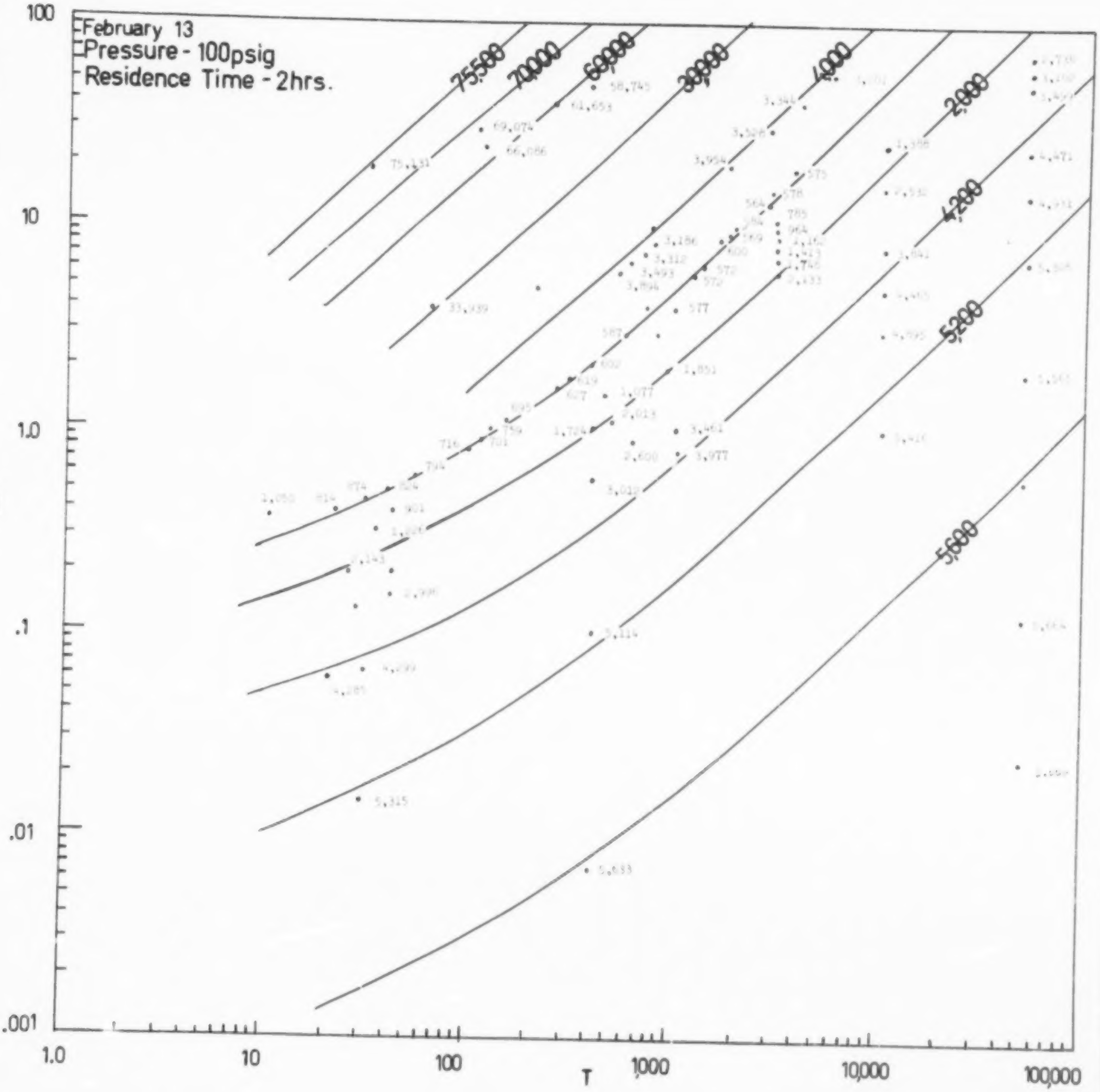

December 13
Pressure - 0.0 psig (1.0 atm.)
Residence Time - 1.08 hrs.
H
T
100
10
1.0
.1
.01
.001
1.0
10
100
1,000
10,000
100,000
105,000
40,000
10,000
1,400
3,000
4,400
4,600
4,720
104,109
39,899
17,550
7,473
7,555
7,758
7,971
8,181
8,552
9,207
1,619
1,166
1,653
1,269
1,732
1,829
1,165
1,230
1,567
1,160
1,159
1,161
1,157
1,155
1,369
1,920
2,007
2,872
3,049
2,329
3,011
3,668
3,937
4,182
4,453
1,743
1,951
2,270
2,594
3,493
3,951
1,025
1,037
1,052
1,062
1,094
1,409
1,907
2,397
3,515
3,904
3,802
4,409
4,685

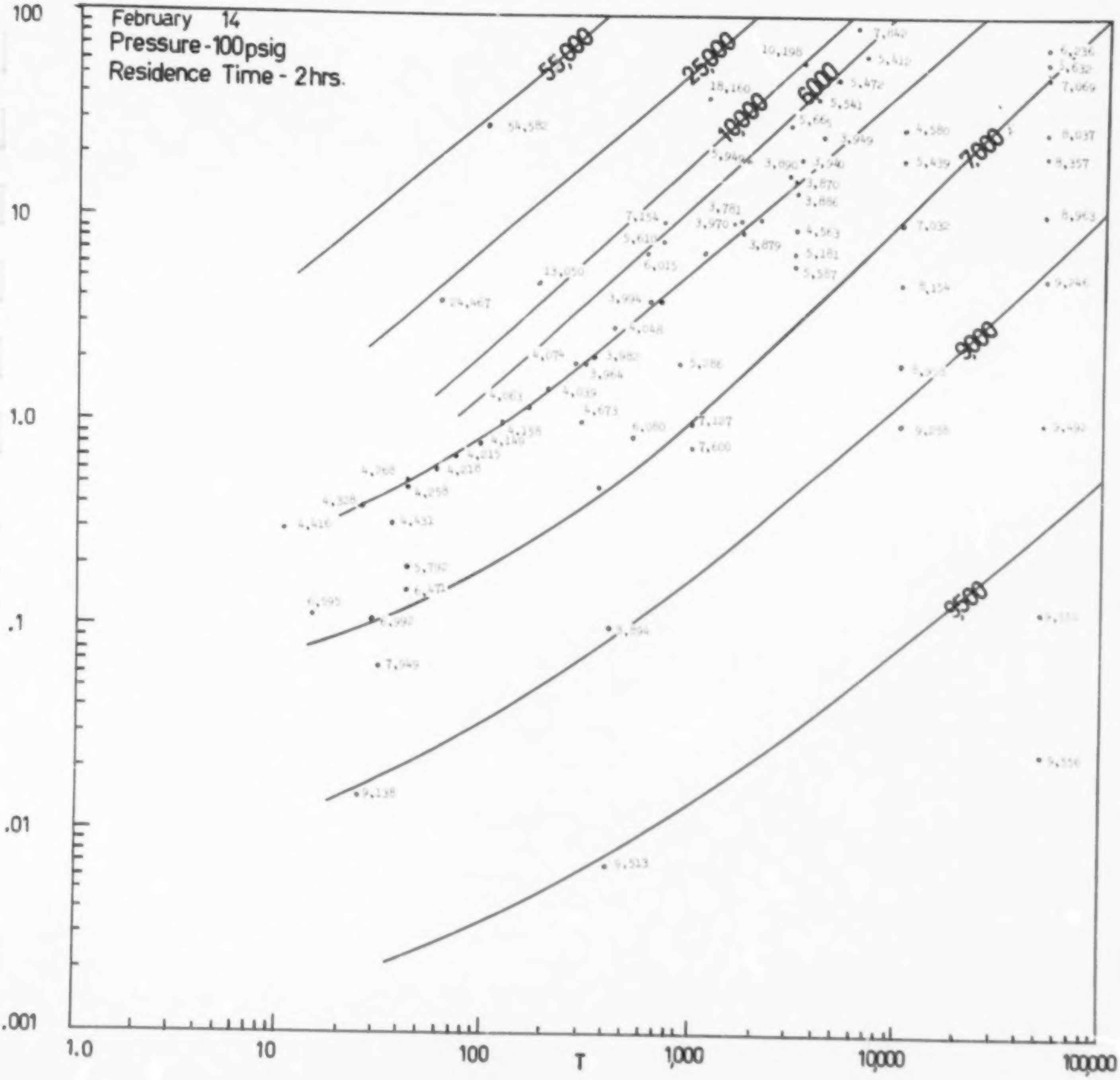

January 5
Pressure - 60psig
Residence Time - 1.0 hr.
69,000
25,000
23,000
3,400
500
650
900
1,100
1195
68,706
29,356
21,755
22,036
25,515
14,062
2,682
2,761
2,919
3,318
418
474
278
369
496
758
906
1,075
1,138
480
534
604
681
854
1,019
1,098
1,149
1,175
1,187
1,197
1,206
1,261
279
297
281
280
283
546
489
745
790
574
308
309
301
292
296
290
289
330
442
454
565
621
743
861
922
1,101
1,111
1,192
100
10
1.0
.1
.01
.001
H
10
100
T
1,000
10,000
100,000

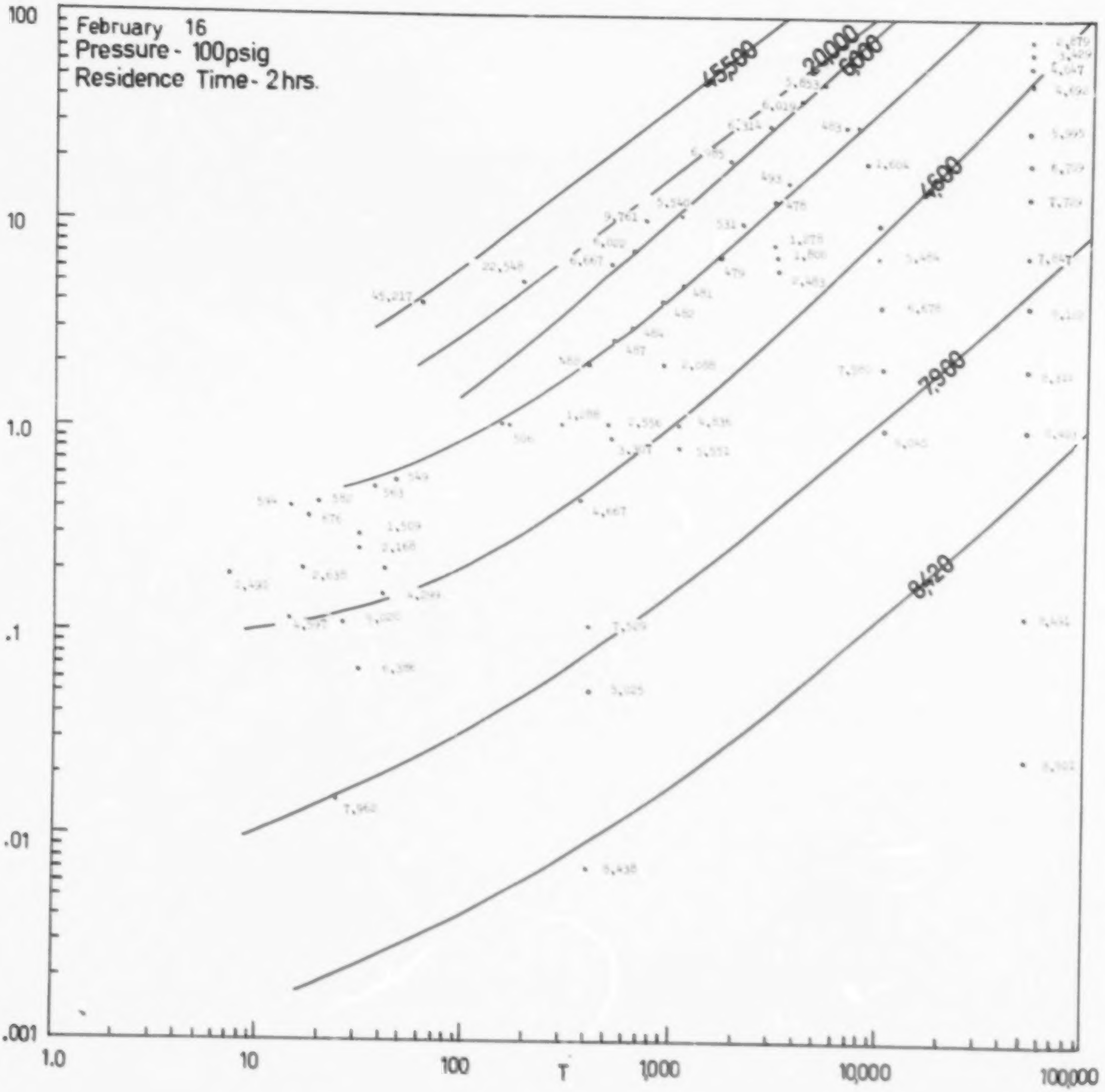

January 10
Pressure - 60psig
Residence Time - 2.19 hrs.
66000
30000
24000
1800
4300
6000
7100
21,154
21,477
22,320
23,505
27,983
23,512
66,621
6,268
6,451
1,464
1,347
7,042
1,495
1,917
1,534
1,510
1,615
1,351
2,960
4,188
1,348
1,350
1,449
1,694
2,146
2,872
3,302
5,545
1,337
1,338
1,336
1,333
1,392
1,329
1,327
1,315
1,318
1,294
1,296
1,238
1,239
1,237
1,251
1,435
1,790
4,057
3,975
5,996
7,095
100
10
1.0
.1
.01
.001
1.0
10
100
T
1,000
10,000
100,000

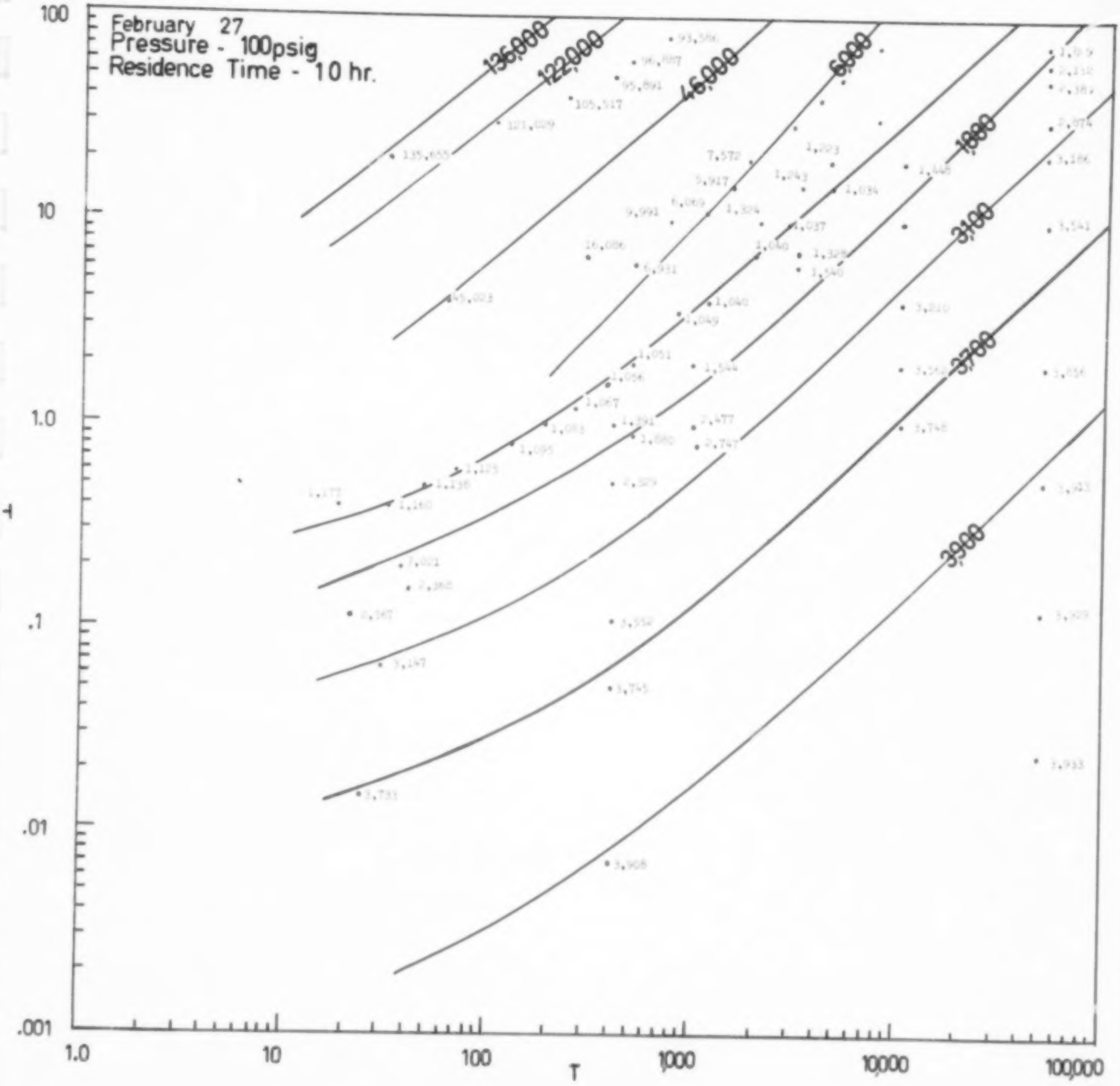


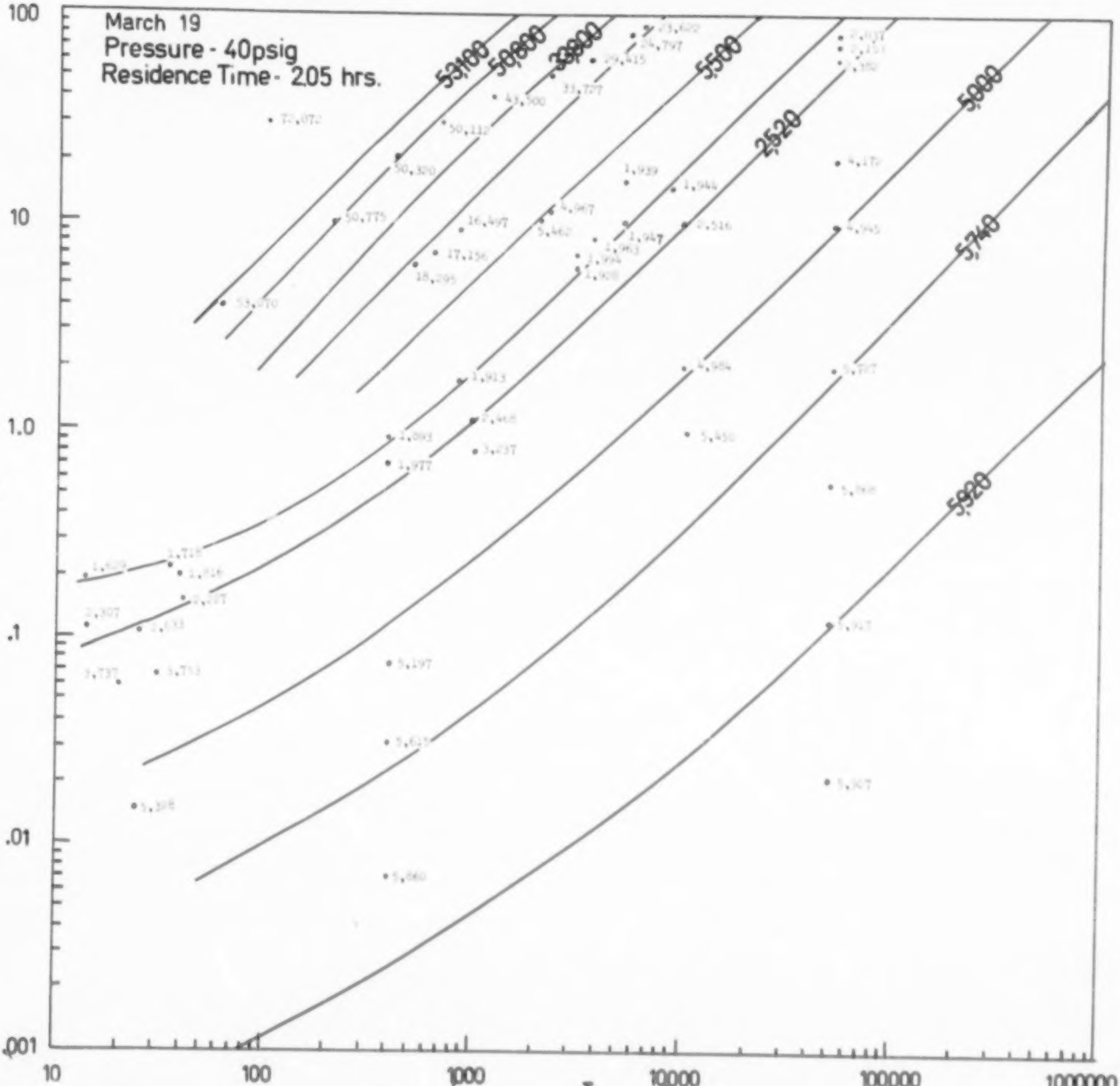
January 11
Pressure - 60psig
Residence Time - 2.19 hrs.
78,000
45,000
20,000
8,000
1,700
3200
3600
77,321
44,009
25,255
16,646
12,589
10,767
9,993
19,886
8,055
9,956
1,431
1,242
1,195
7,943
1,158
269
572
1,254
1,828
824
1,098
1,412
2,541
3,054
3,277
3,449
2,508
3,053
3,334
3,578
3,612
3,629
3,635
264
263
264
263
265
263
266
267
270
358
652
276
277
277
1,288
1,850
286
493
293
877
298
1,357
360
339
327
318
474
658
817
717
1,084
2,359
1,771
3,008
2,228
2,233
3,324
3,269
100
10
1.0
.1
.01
.001
1.0
10
100
T
1,000
10,000
100,000

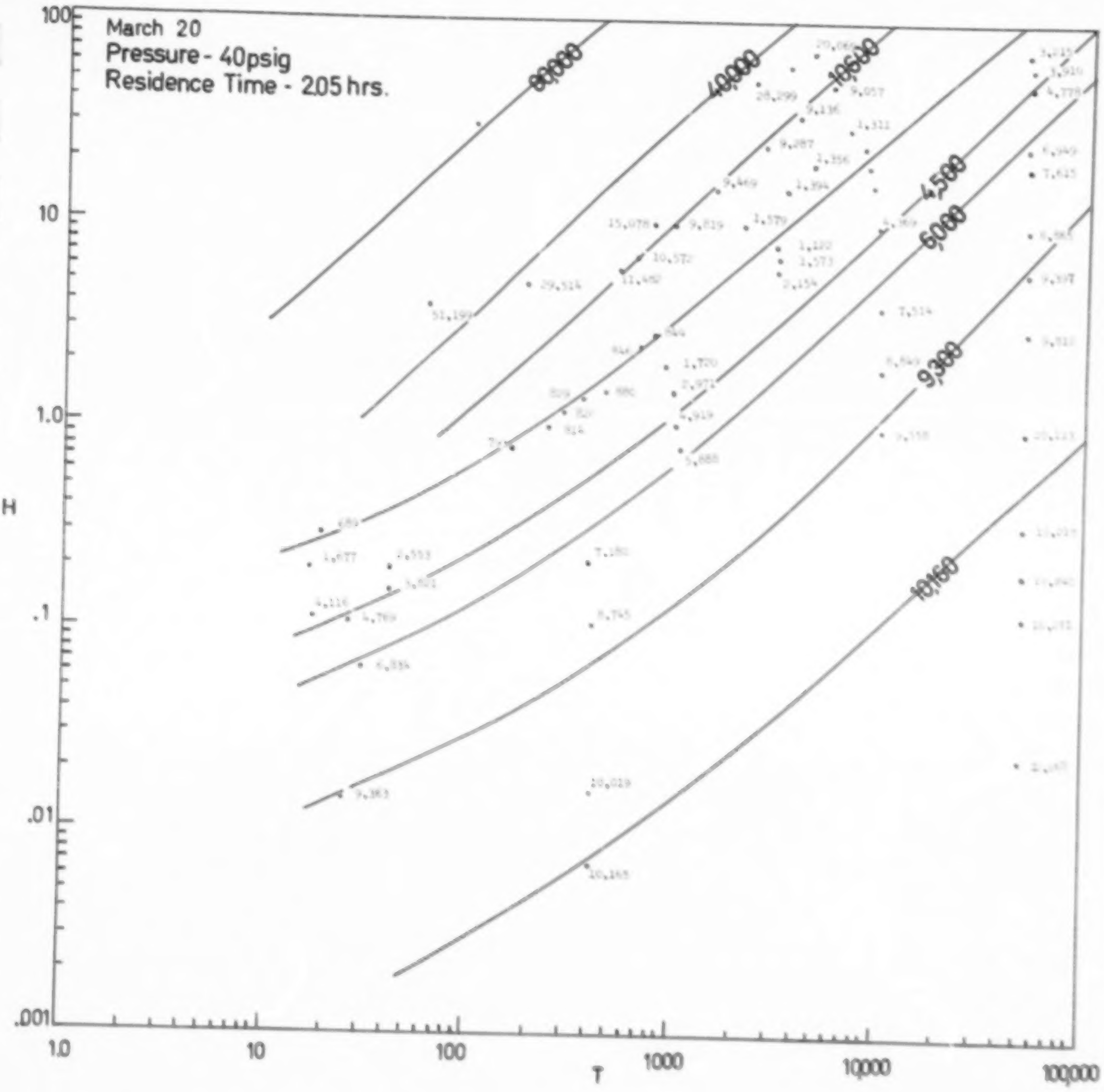
February 13
Pressure - 100psig
Residence Time - 2hrs.
75,500
70,000
60,000
30,000
4,000
2,000
4,200
5,200
5,600
75,131
69,074
66,086
61,653
58,745
33,939
3,344
3,528
3,954
3,186
3,312
3,493
3,894
575
578
564
584
569
600
572
572
785
964
1,162
1,413
1,746
2,133
577
587
602
619
627
695
759
701
716
794
824
874
814
1,050
901
1,026
2,143
2,996
1,077
2,013
1,724
1,851
3,461
2,600
3,977
3,012
3,114
4,299
4,285
5,325
5,633
1,398
2,532
3,841
4,895
3,416
2,739
3,102
3,499
4,471
4,931
1,561
H
T
100
10
1.0
.1
.01
.001
1.0
10
100
1,000
10,000
100,000

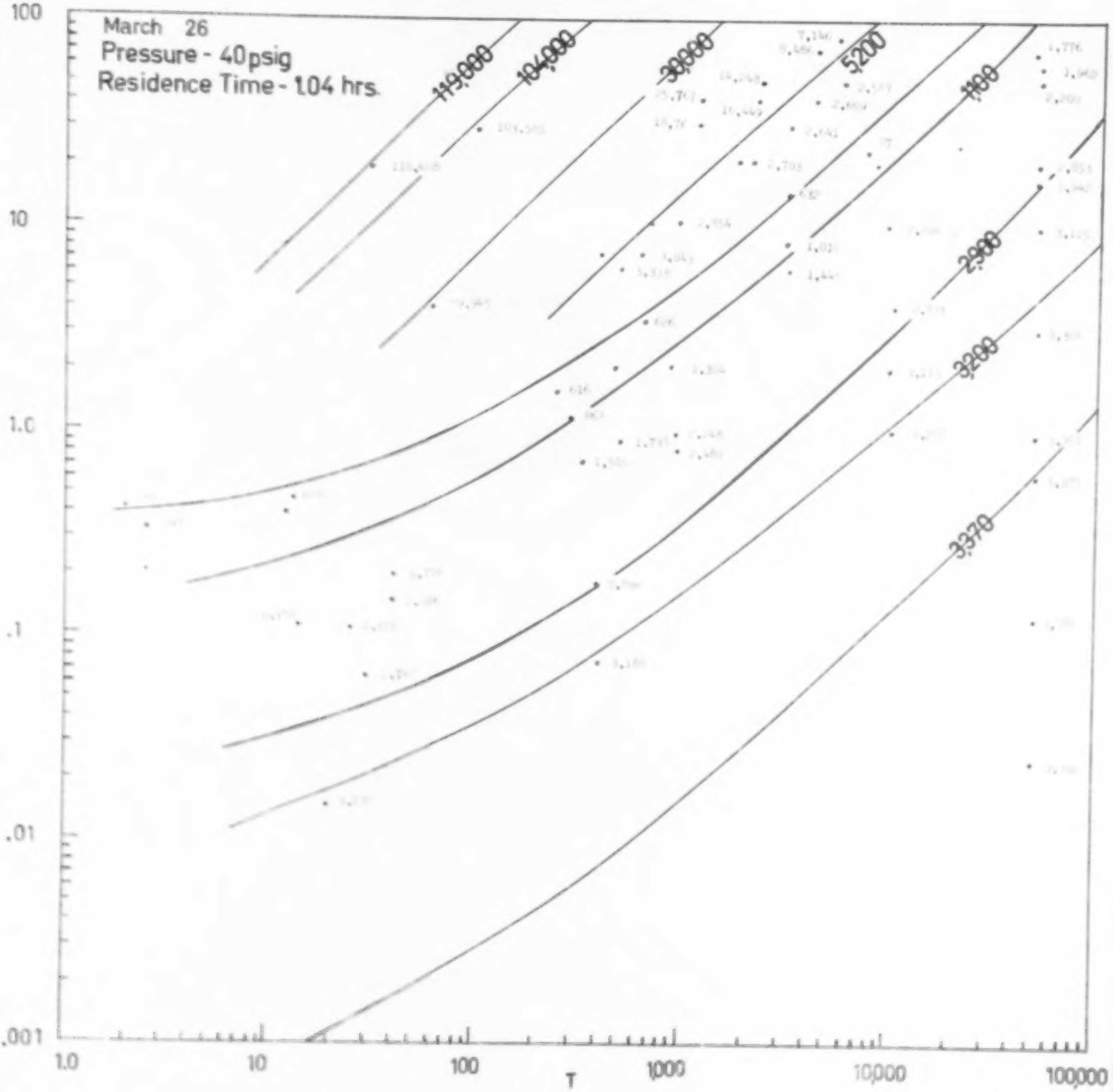

February 14
Pressure - 100 psig
Residence Time - 2 hrs.
55,000
25,000
10,000
6000
7000
9000
9500
54,582
24,467
18,160
13,050
10,198
7,842
5,412
5,472
5,541
5,666
3,949
5,949
3,890
3,940
3,870
3,886
4,580
5,439
6,236
5,632
7,069
8,037
8,357
7,154
5,610
6,015
3,781
3,970
3,879
4,563
5,181
5,587
7,032
8,963
8,154
9,246
3,994
4,048
4,074
3,982
3,964
5,286
4,063
4,039
4,673
4,158
4,140
4,215
4,218
6,080
7,127
7,600
9,298
9,490
4,268
4,258
4,328
4,416
4,431
5,792
6,471
6,595
6,992
7,949
8,894
9,134
9,138
9,356
9,513
100
10
1.0
.1
.01
.001
1.0
10
100
1,000
10,000
100,000
T

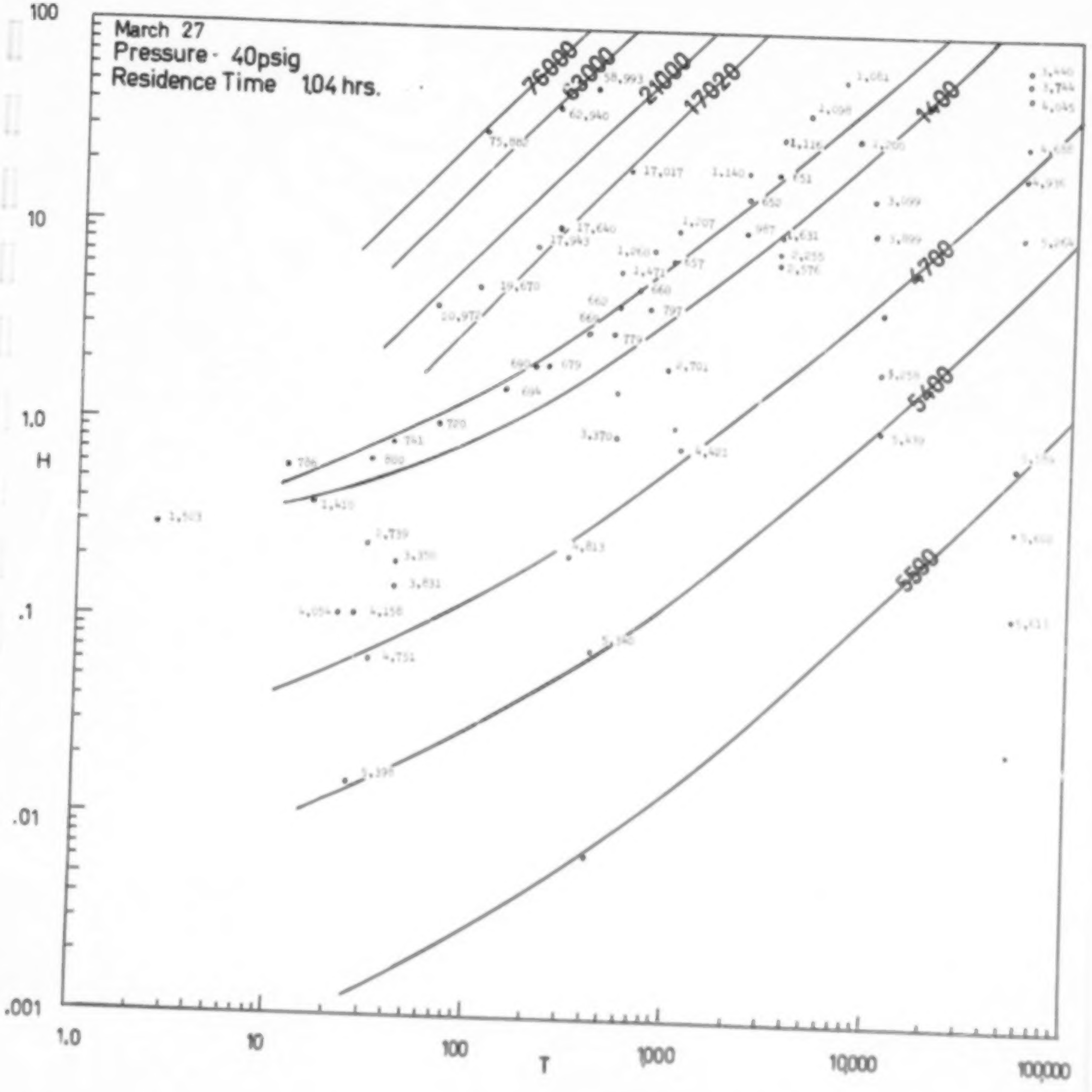

February 16
Pressure - 100psig
Residence Time - 2hrs.
45590
20000
6000
4690
7990
8420
100
10
1.0
.1
.01
.001
1.0
10
100
T
1000
10,000
100,000
45,217
22,548
6,667
6,022
9,761
5,540
6,985
6,324
6,019
5,853
483
493
478
531
479
481
482
484
487
1,078
1,800
2,483
1,604
506
1,088
2,556
3,307
4,536
3,552
2,088
549
563
582
594
676
1,509
2,168
2,635
2,490
4,299
4,597
3,020
6,396
4,667
7,529
5,025
7,962
8,438
5,484
4,678
7,380
9,045
2,879
3,429
4,047
4,690
5,995
6,759
7,709
7,647

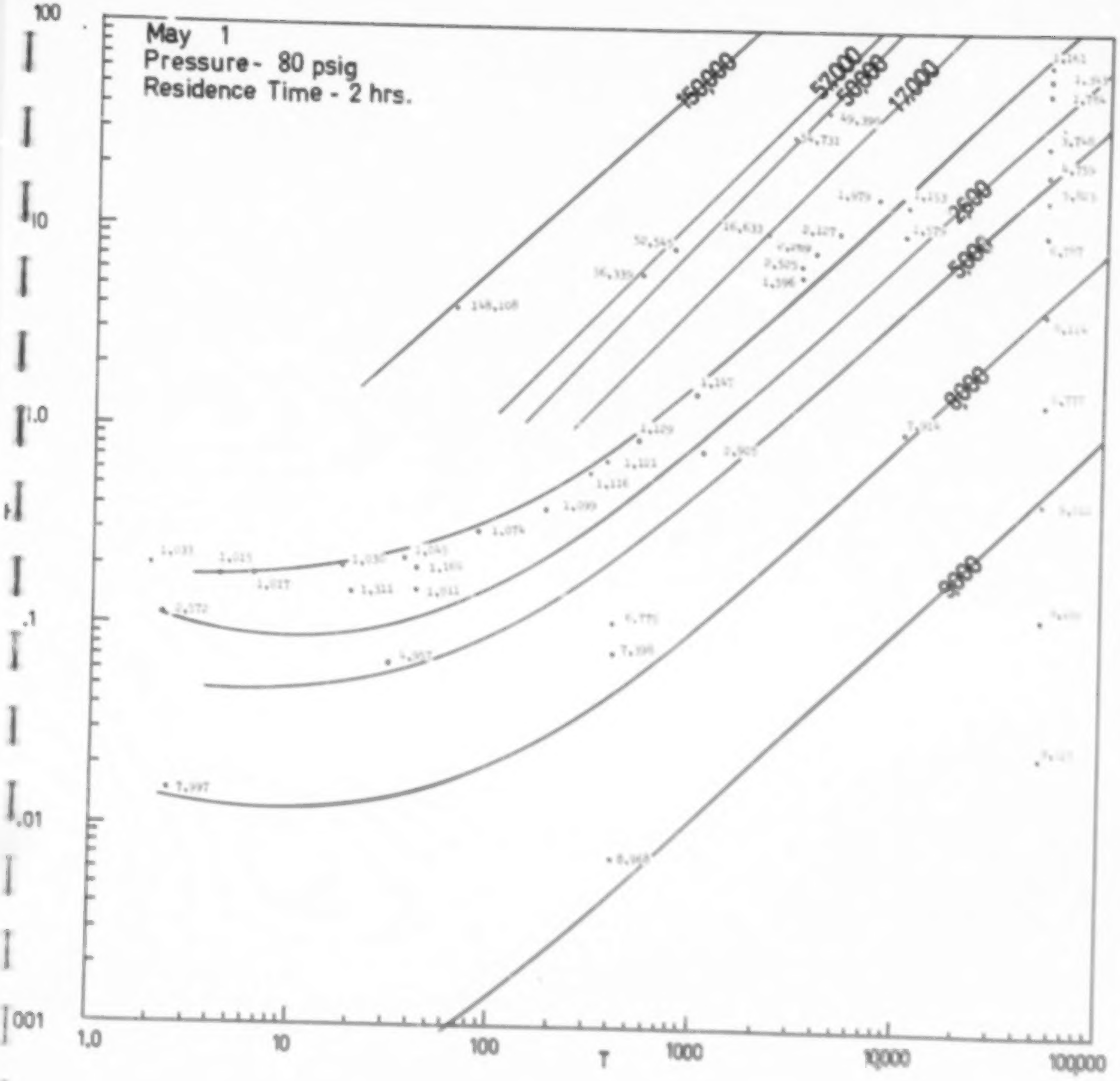

February 27
Pressure - 100psig
Residence Time - 10 hr.
136,000
122,000
46,000
6000
1800
3100
3700
3900
135,655
121,029
105,517
95,891
96,887
93,586
45,023
16,086
9,991
6,069
6,931
7,572
5,917
1,324
1,223
1,243
1,034
1,037
1,040
1,328
1,540
1,446
1,040
1,049
1,051
1,056
1,067
1,083
1,095
1,125
1,138
1,160
1,177
1,544
1,391
1,880
2,477
2,747
2,329
2,001
2,360
2,367
3,147
3,552
3,745
3,733
3,908
3,210
3,552
3,748
2,212
2,381
2,874
3,186
3,541
3,923
3,933
H
T
100
10
1.0
.1
.01
.001
1.0
10
100
1000
10,000
100,000


March 19
Pressure - 40psig
Residence Time - 2.05 hrs.
53,100
50,800
38,800
5,500
2,520
5,000
5,740
5,920
72,072
50,112
50,320
50,775
53,070
43,500
33,727
29,415
24,797
16,497
17,156
18,295
4,967
5,462
1,939
1,944
1,947
1,963
1,994
2,516
4,945
4,984
1,913
2,468
1,977
5,450
1,718
2,307
3,737
5,197
5,615
5,860
H
100
10
1.0
.1
.01
.001
T
10
100
1000
10,000
100,000
1,000,000

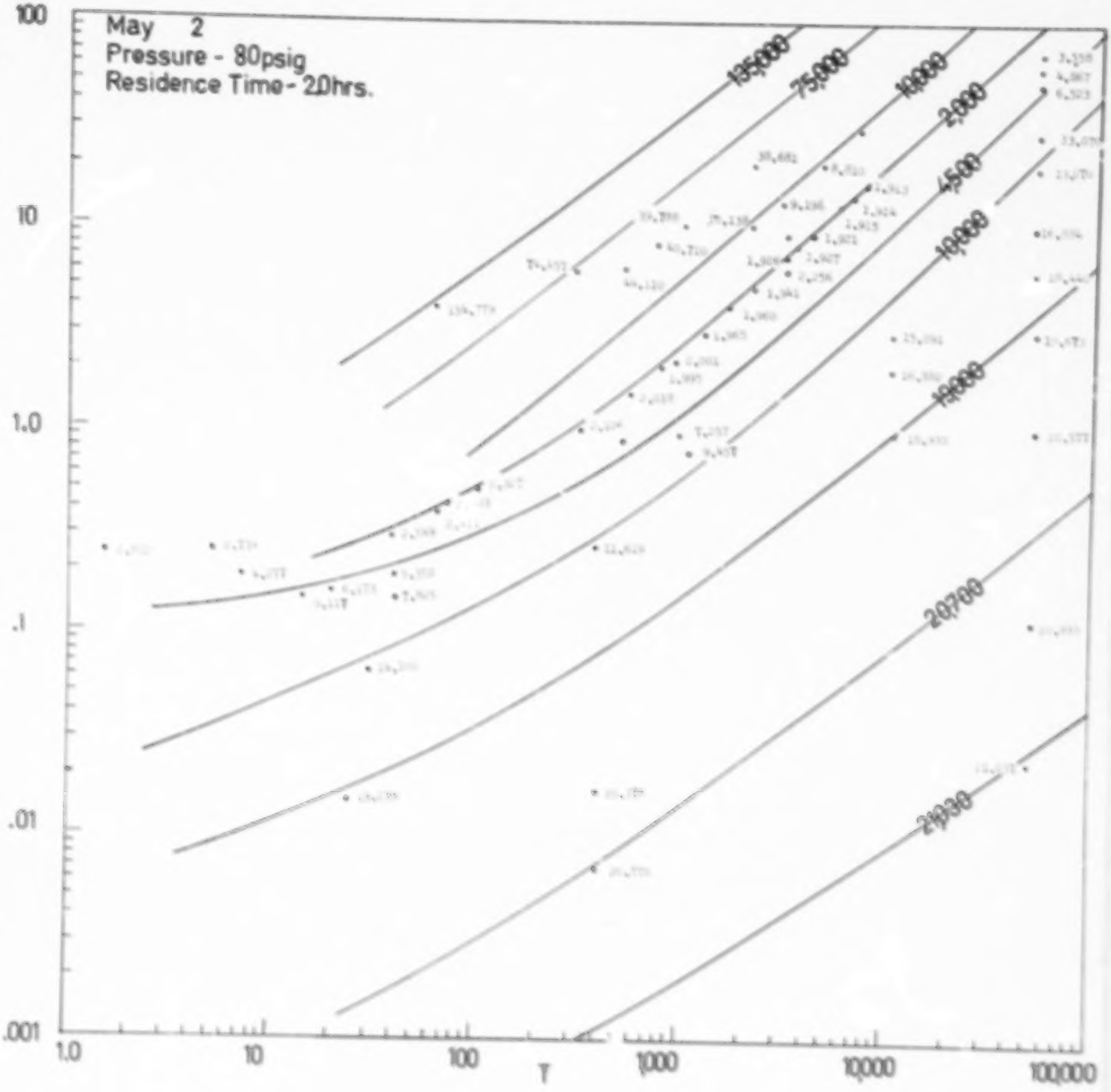

March 20
Pressure - 40psig
Residence Time - 2.05 hrs.
80,000
40,000
10,600
4,500
6,000
9,300
10,160
H
T
100
10
1.0
.1
.01
.001
1.0
10
100
1000
10,000
100,000
51,199
29,514
15,078
9,819
10,572
11,482
9,469
28,299
20,066
9,057
9,136
9,287
1,311
1,356
1,394
1,579
1,122
1,573
2,154
7,514
844
846
1,770
2,971
4,919
5,888
809
886
820
814
689
1,677
2,553
3,621
4,116
4,769
6,336
7,180
8,745
9,363
10,029
10,165
3,215
3,910
4,778
6,949
7,615
9,397
9,158
10,113

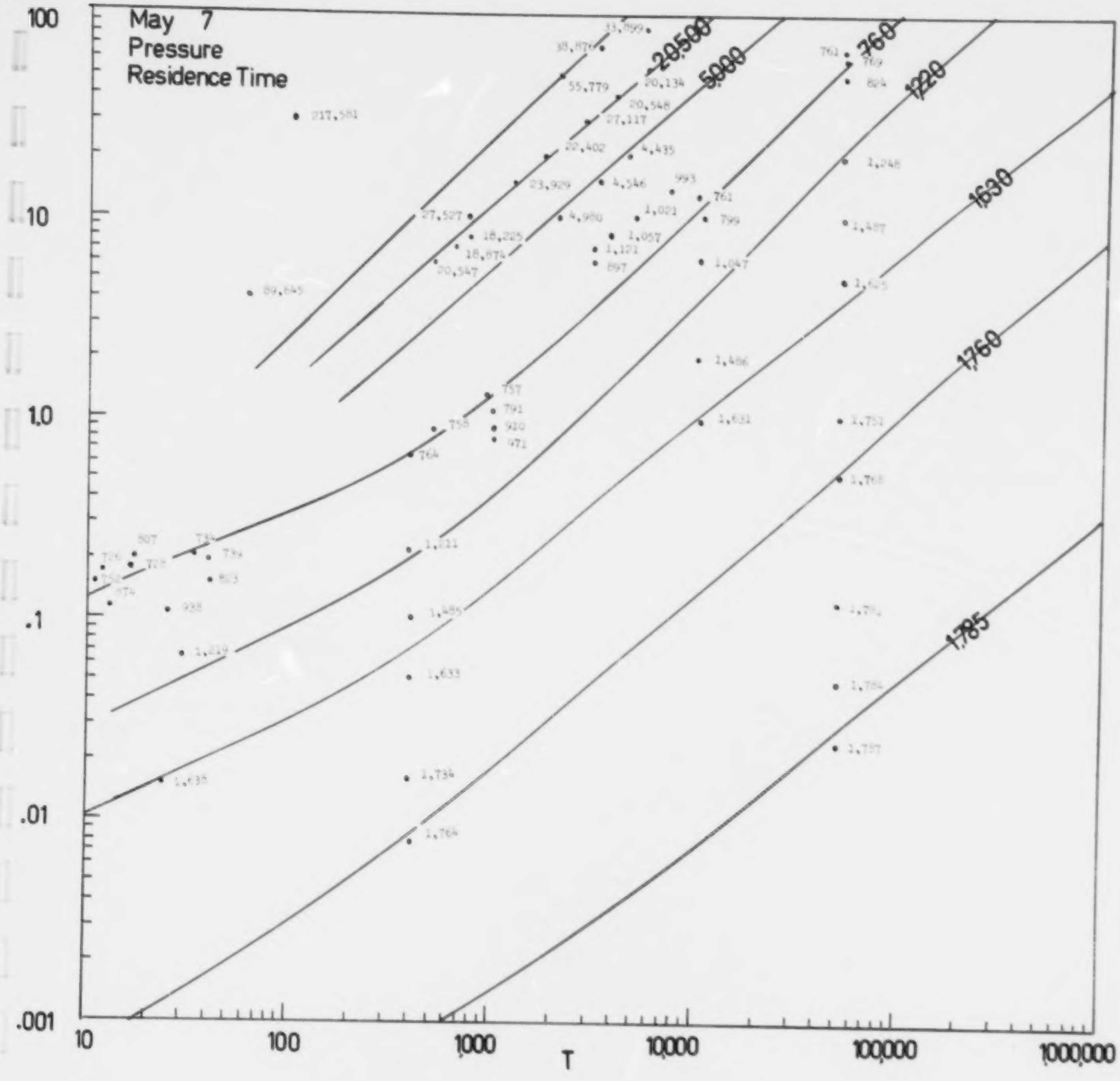

March 26
Pressure - 40 psig
Residence Time - 1.04 hrs.
119,000
104,000
38,000
5200
1100
2900
3200
3370
100
10
1.0
.1
.01
.001
1.0
10
100
1,000
10,000
100,000
T


March 27
Pressure - 40psig
Residence Time 1.04 hrs.
76000
63000
21000
17020
1400
4700
5400
5590
100
10
1.0
H
.1
.01
.001
1.0
10
100
T
1000
10,000
100,000
75,982
62,940
58,993
17,017
17,640
17,943
19,670
20,972
1,140
1,116
1,098
1,081
651
650
987
1,631
2,255
2,576
1,207
1,260
1,471
657
660
662
669
797
779
690
679
694
720
741
786
880
1,410
1,503
2,701
3,370
4,421
1,739
3,350
3,831
4,054
4,158
4,751
4,813
5,390
3,099
3,899
3,259
5,439
3,440
3,744
4,045
4,688
4,936
5,264



May 1
Pressure - 80 psig
Residence Time - 2 hrs.

May 2
Pressure - 80psig
Residence Time - 20hrs.
135,000
75,000
10,000
2,000
4,500
10,000
19,000
20,700
21,030
100
10
1.0
.1
.01
.001
1.0
10
100
1000
10,000
100,000
T

May 7
Pressure
Residence Time
100
10
1.0
.1
.01
.001
10
100
1,000
10,000
100,000
1000,000
T
20500
5000
760
1220
1630
1760
1785
217,581
89,645
33,899
38,876
55,779
20,134
20,548
27,117
22,402
4,435
23,929
4,546
993
761
27,527
4,980
1,021
799
18,225
1,057
18,874
1,171
20,547
897
1,047
761
769
824
1,248
1,487
1,625
1,486
757
791
758
910
971
764
1,631
1,751
1,768
807
734
726
739
752
728
823
674
938
1,211
1,219
1,485
1,633
1,784
1,797
1,635
1,734
1,764

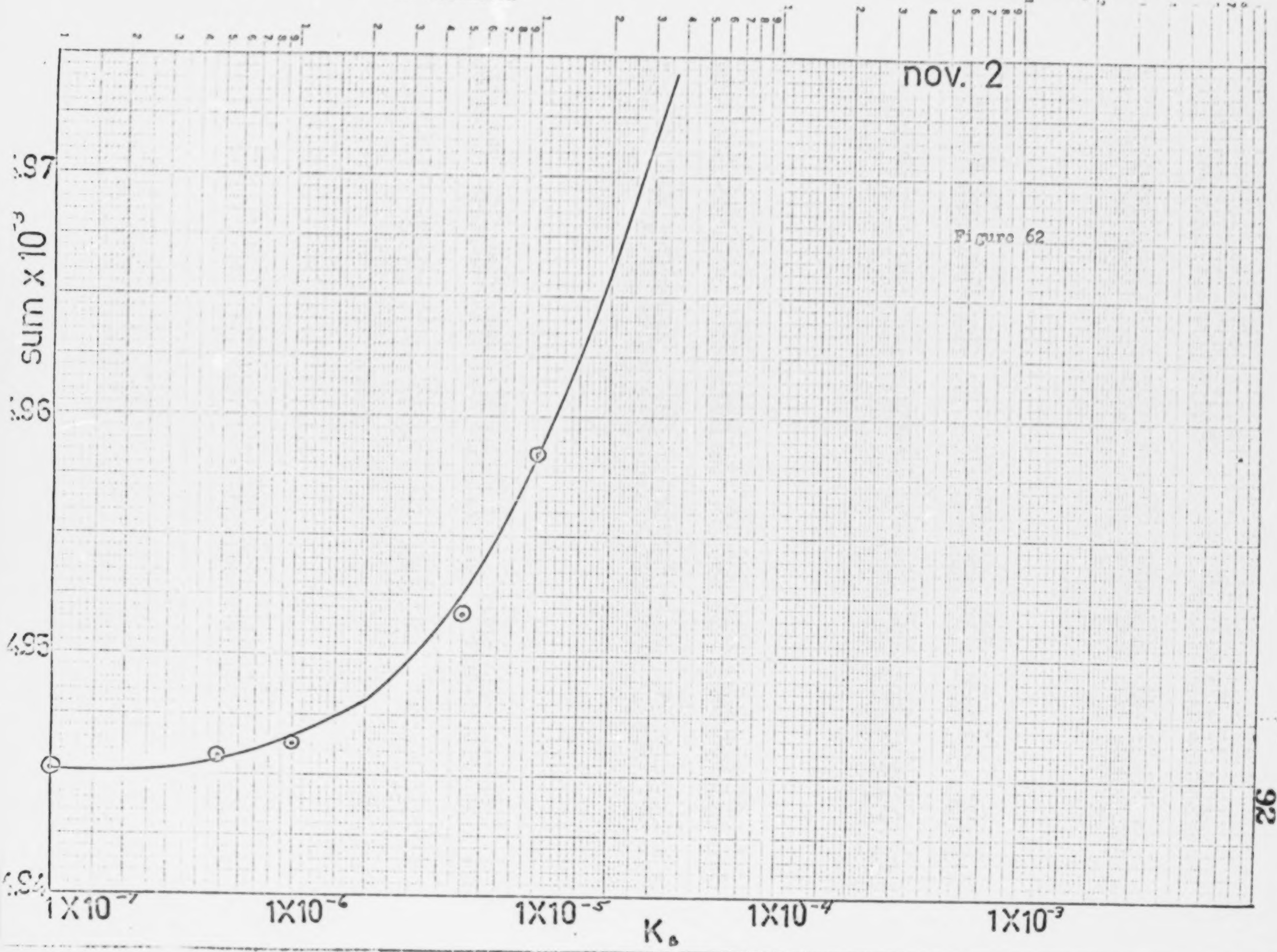

nov. 2
sum x 10^{-3}
4.97
4.96
4.95
4.94
1X10^{-7}
1X10^{-6}
1X10^{-5}
1X10^{-4}
1X10^{-3}
K$_a$

Figure 62

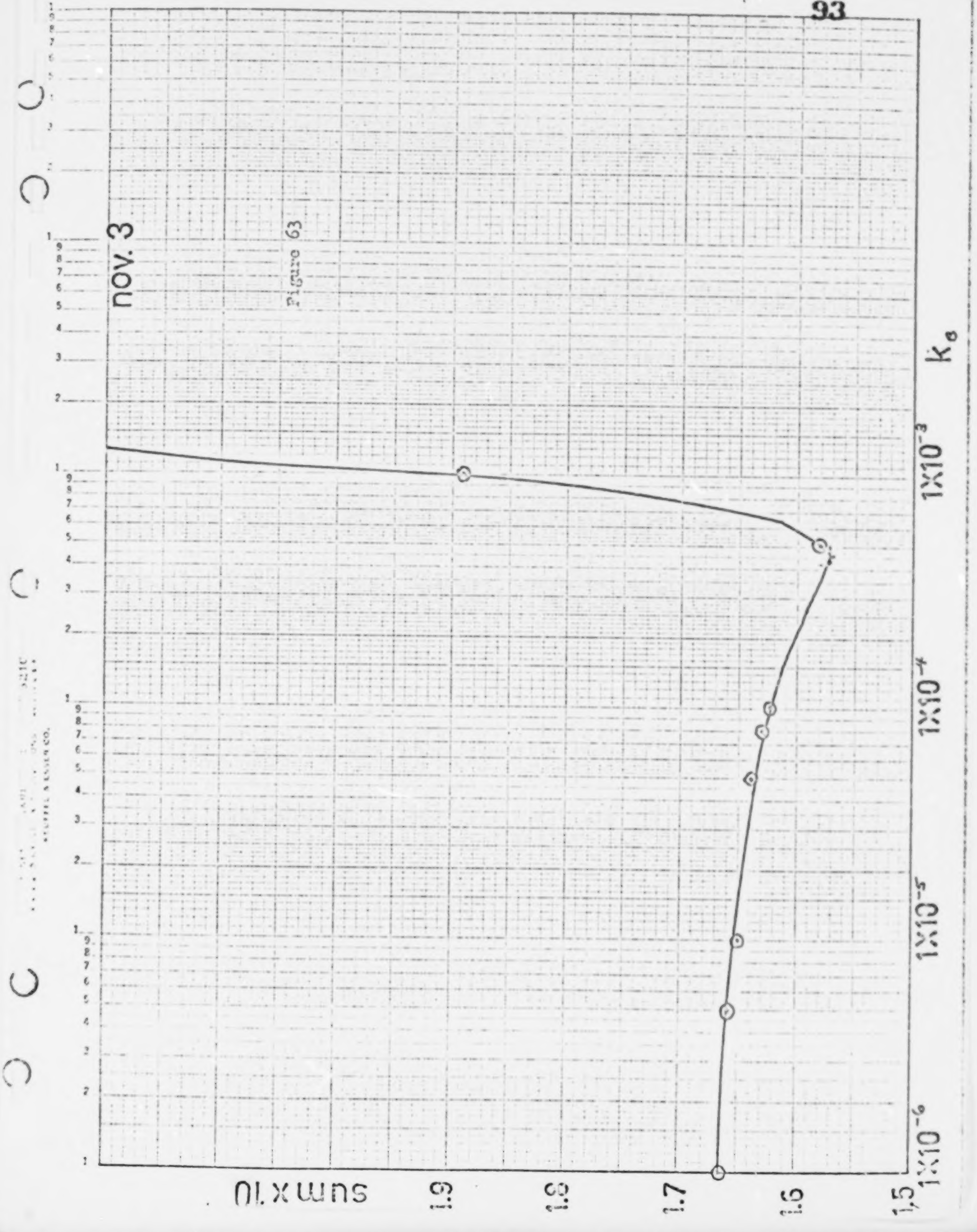


Figure 63

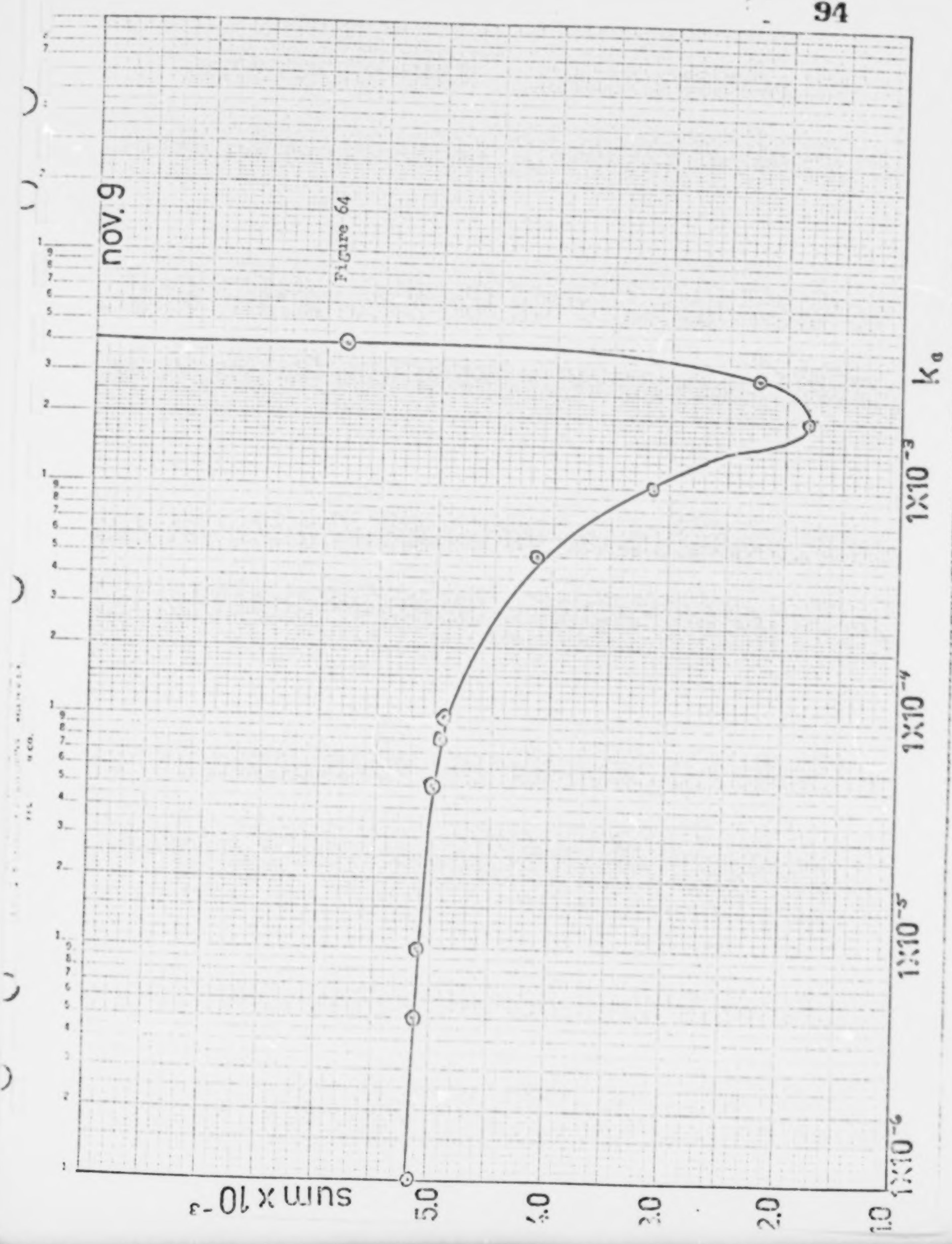


Figure 64

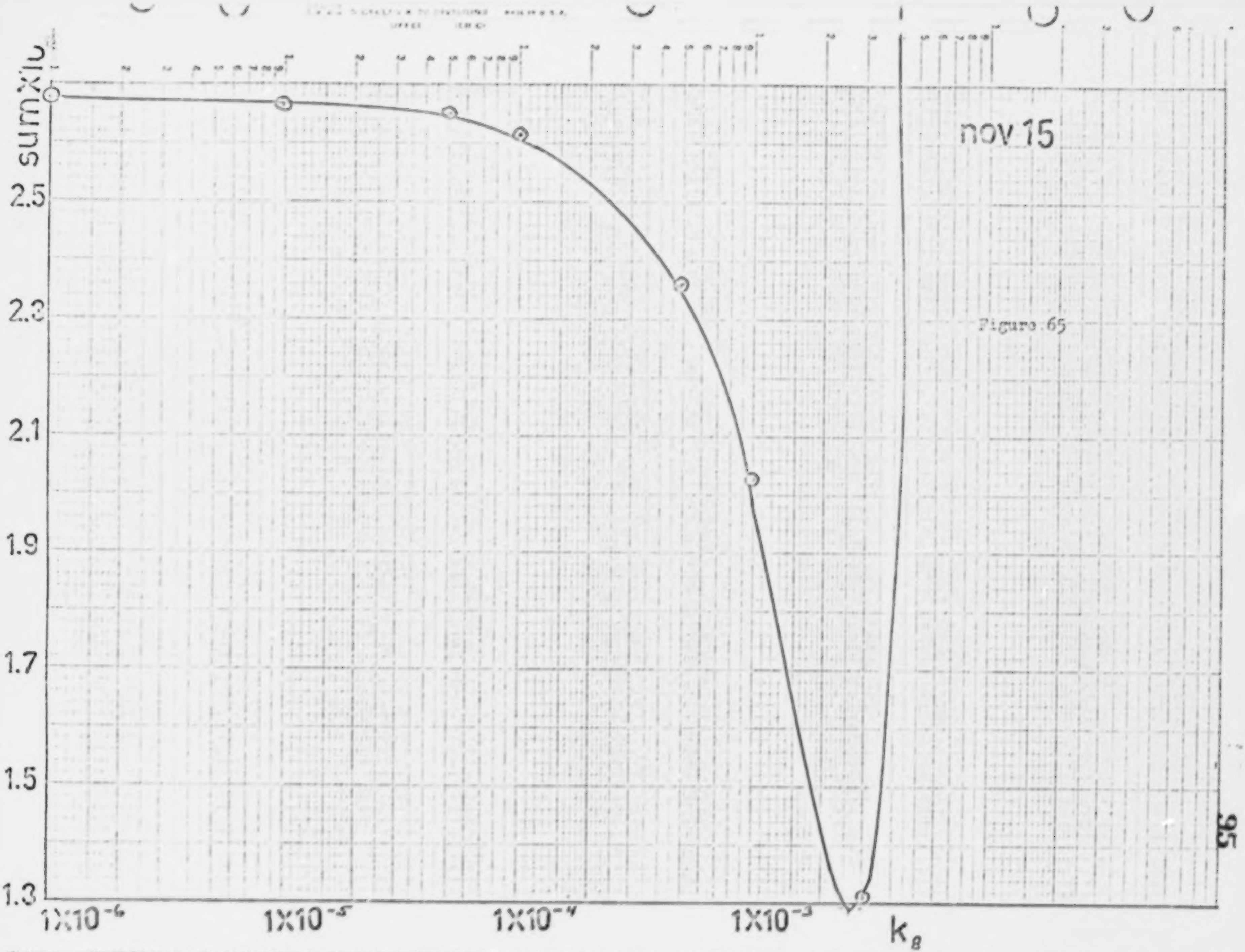
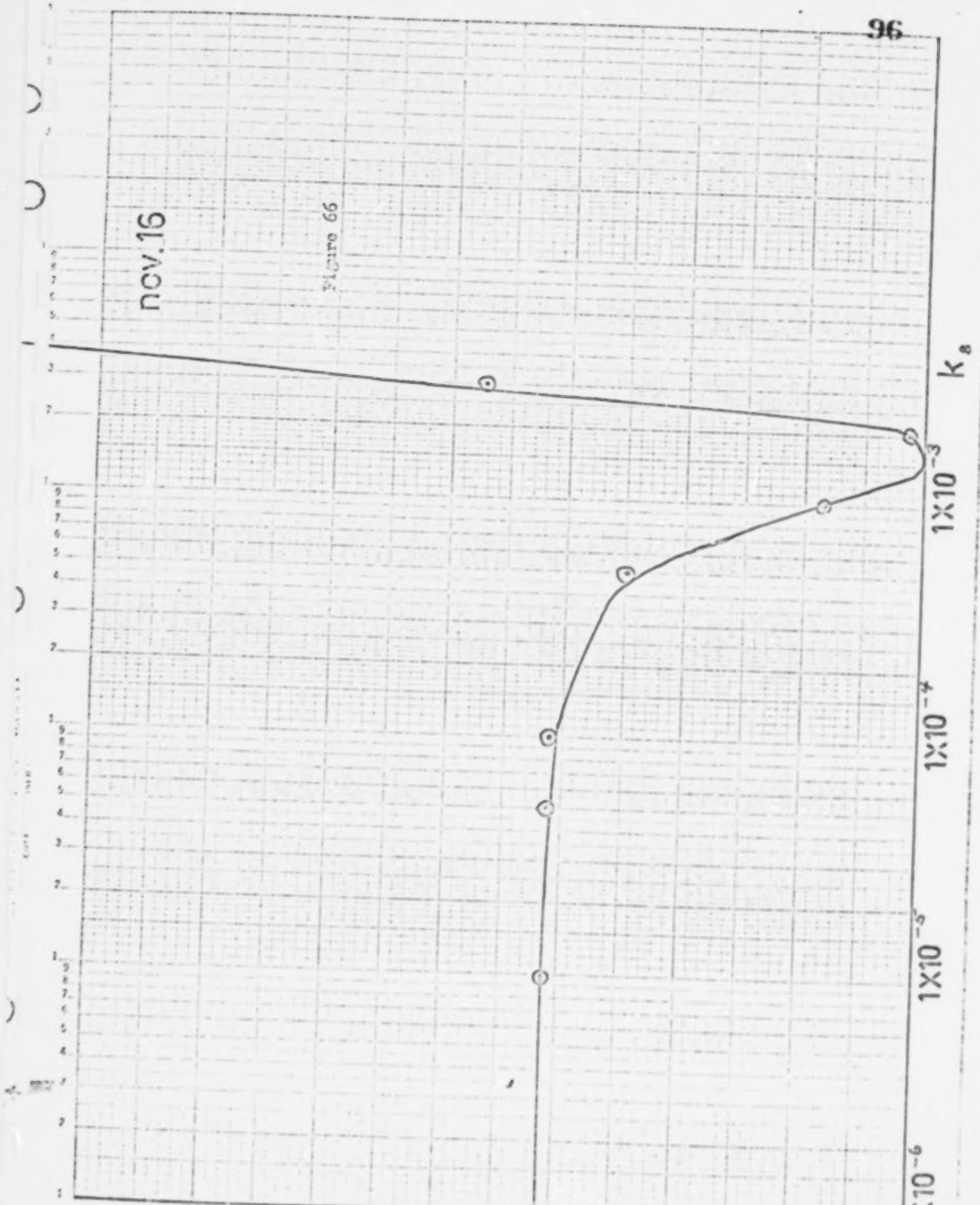


Figure 65


nov.16
Figure 66
k_s
1X10^{-3}
1X10^{-4}
1X10^{-5}
1X10^{-6}
sumx10^{-3}
10.
9.0
8.0
7.0

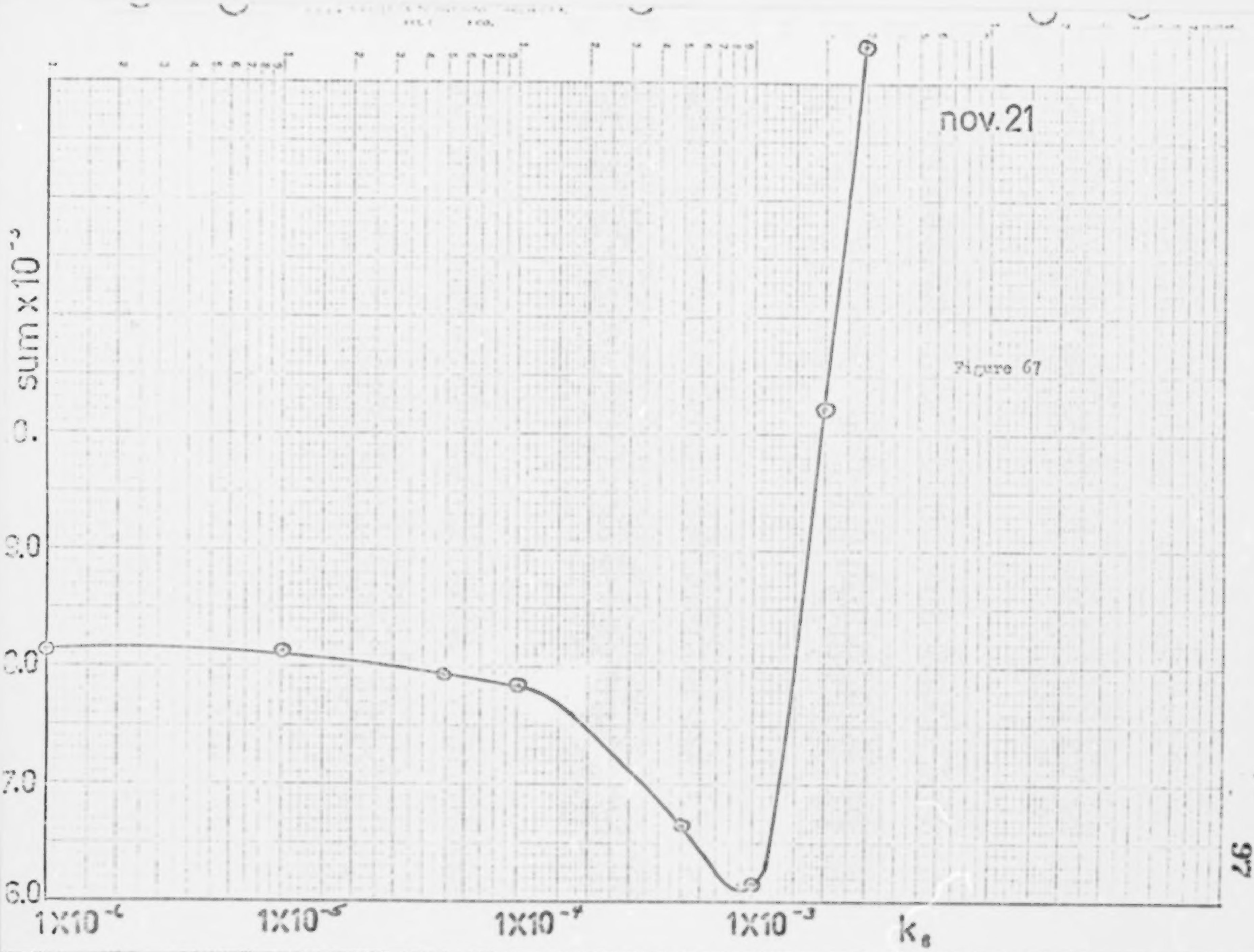


Figure 67

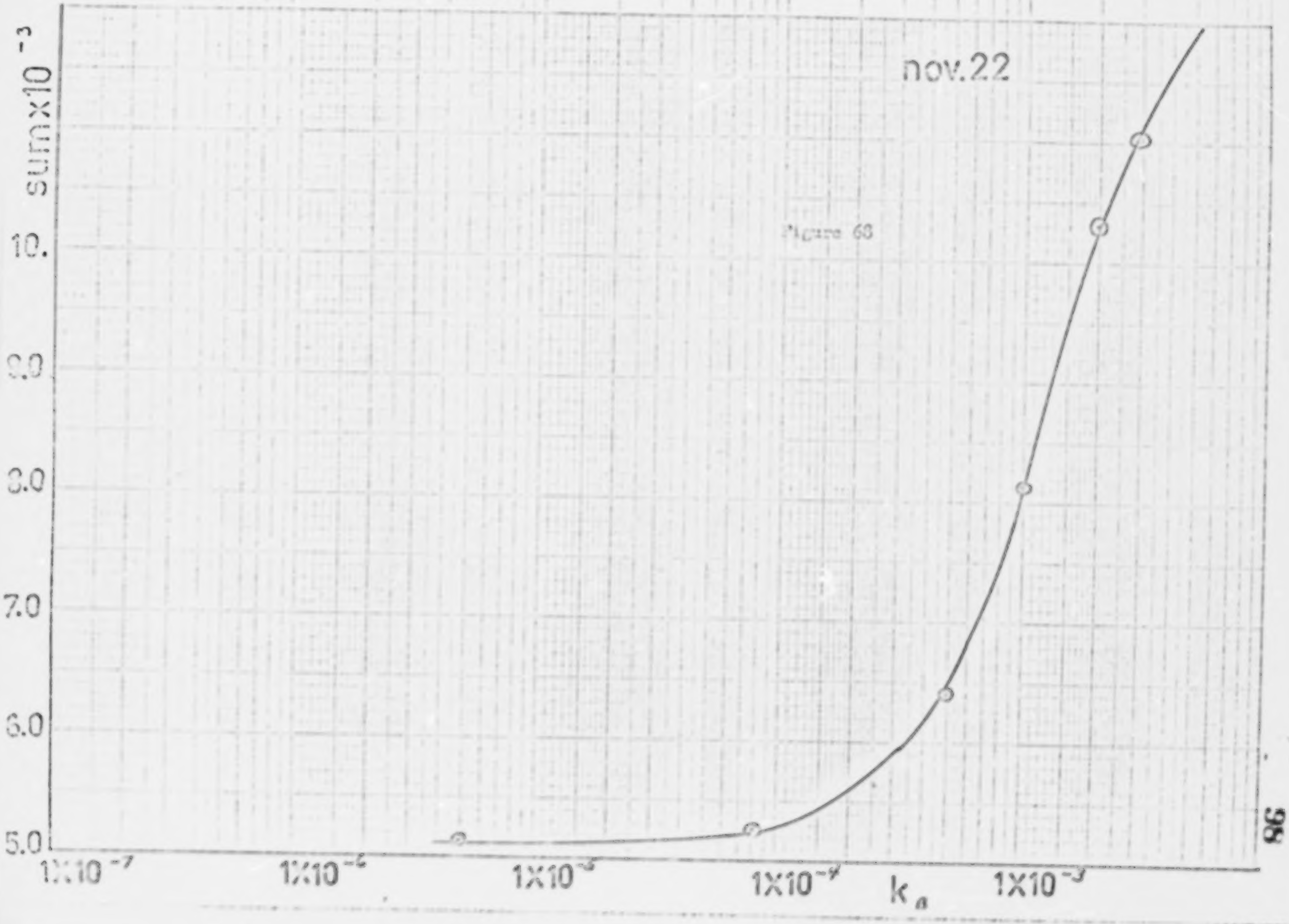
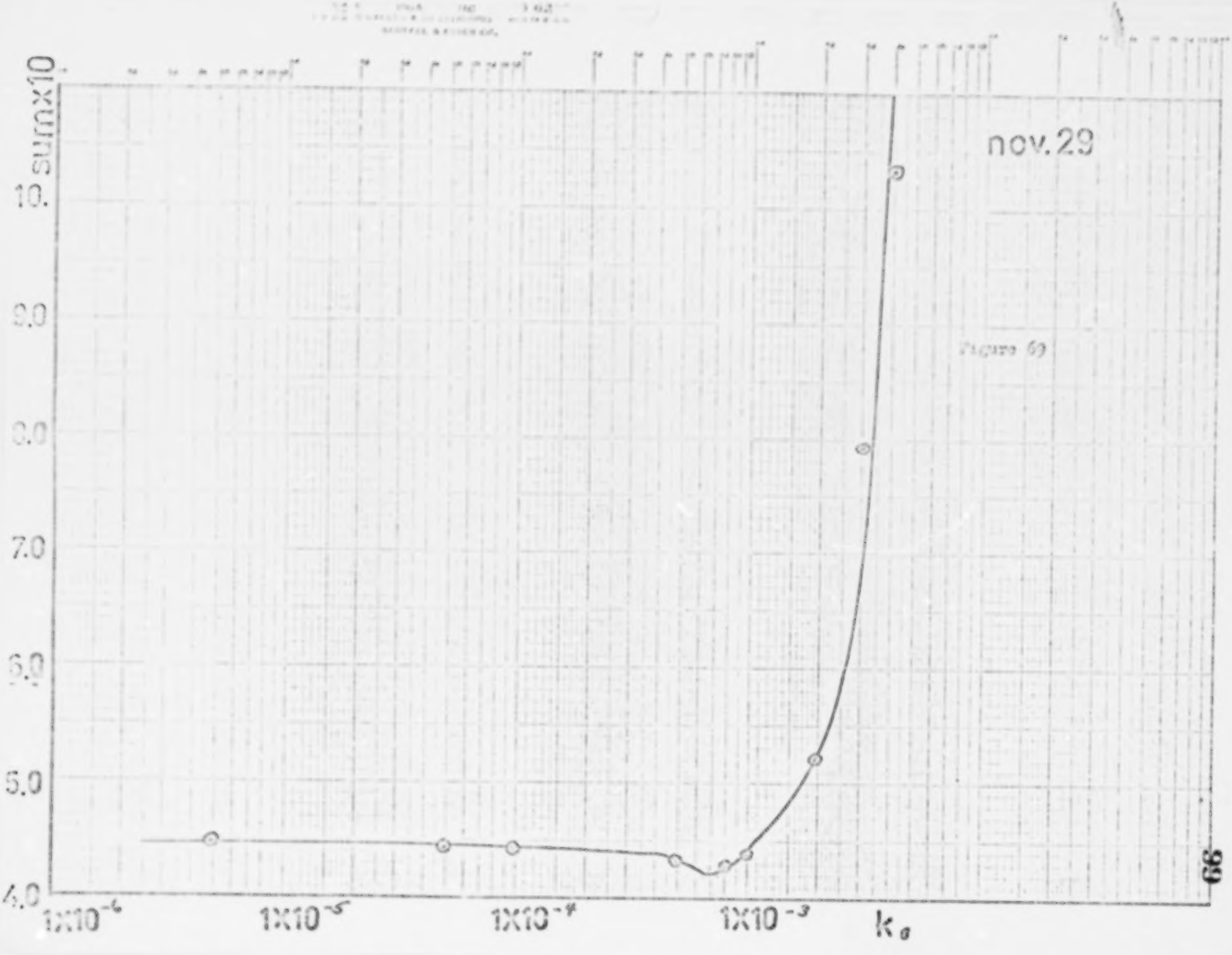

nov.22
sum x10 $^{-3}$
10.
9.0
8.0
7.0
6.0
5.0
1X10 $^{-7}$
1X10 $^{-6}$
1X10 $^{-5}$
1X10 $^{-4}$
1X10 $^{-3}$
k_a

Figure 68



nov.29

Figure 69

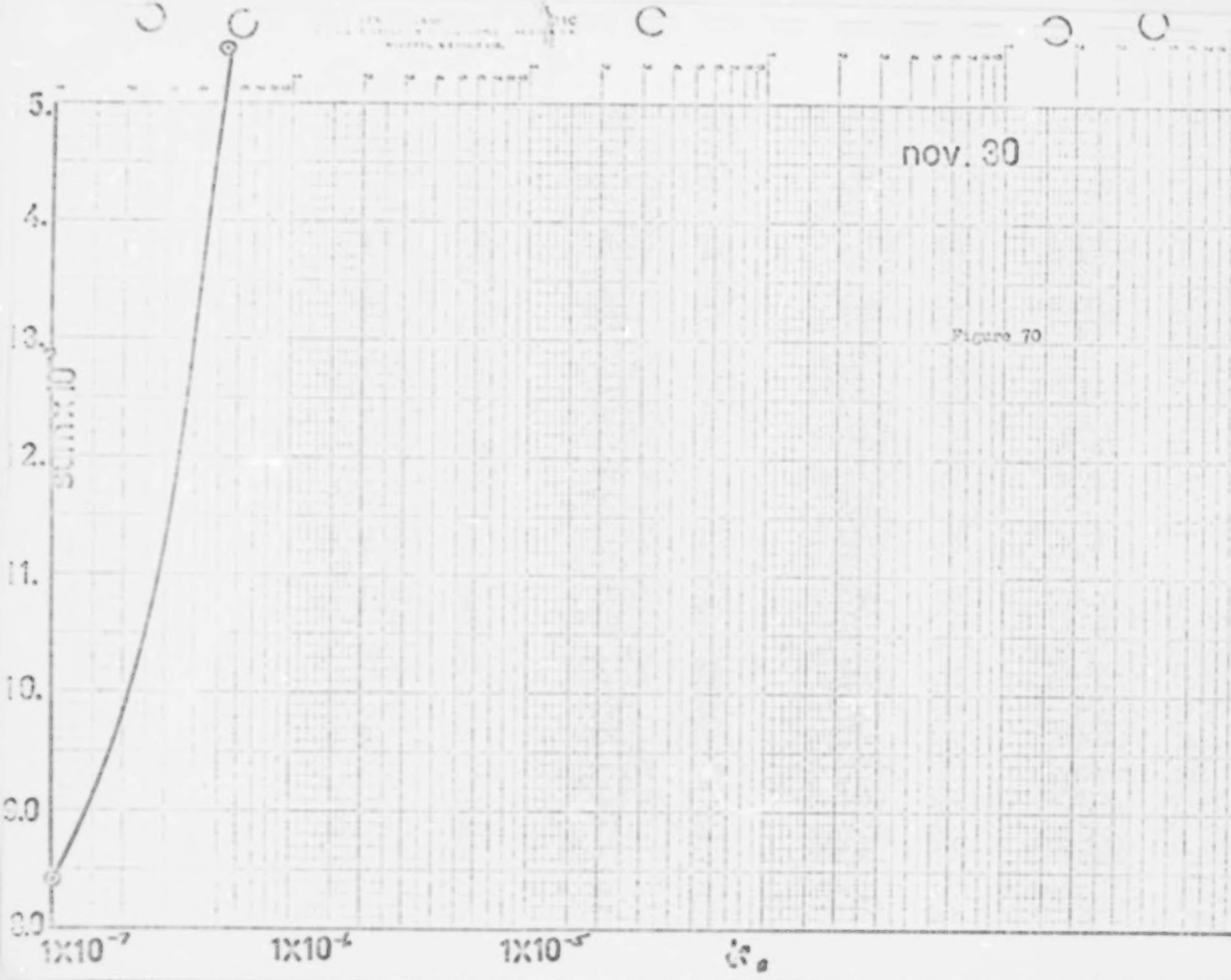


Figure 70

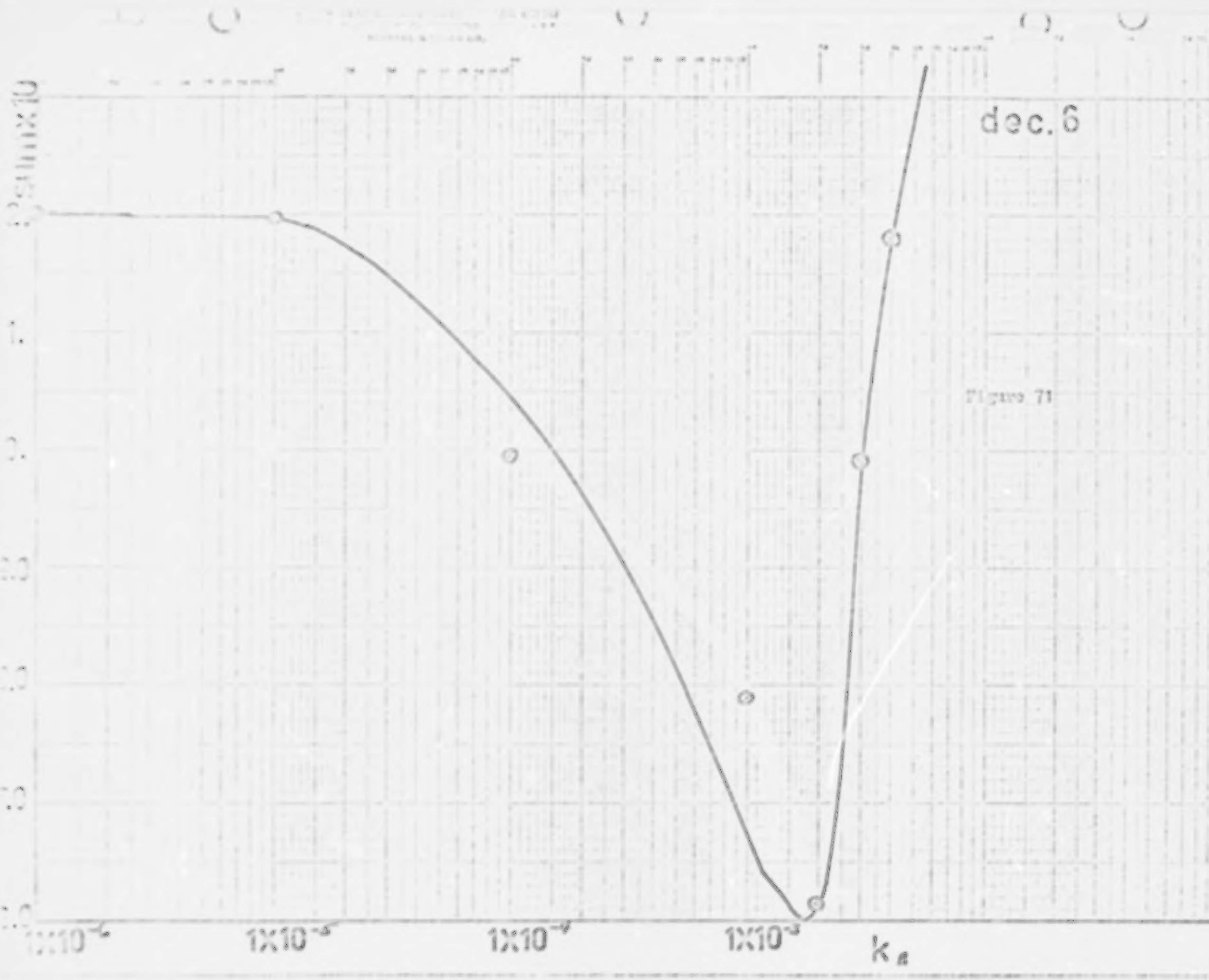
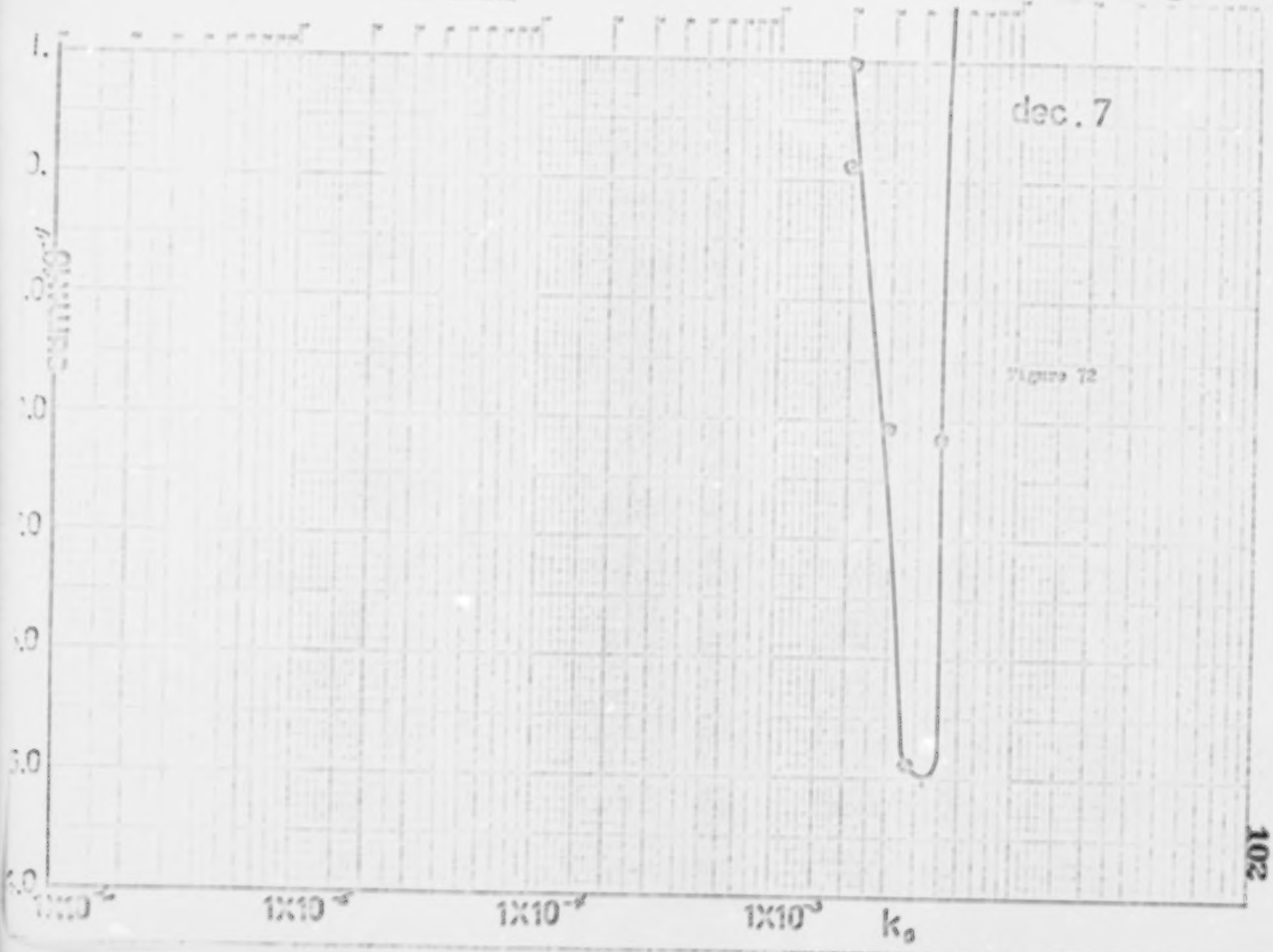


Figure 71



dec. 7

Figure 72

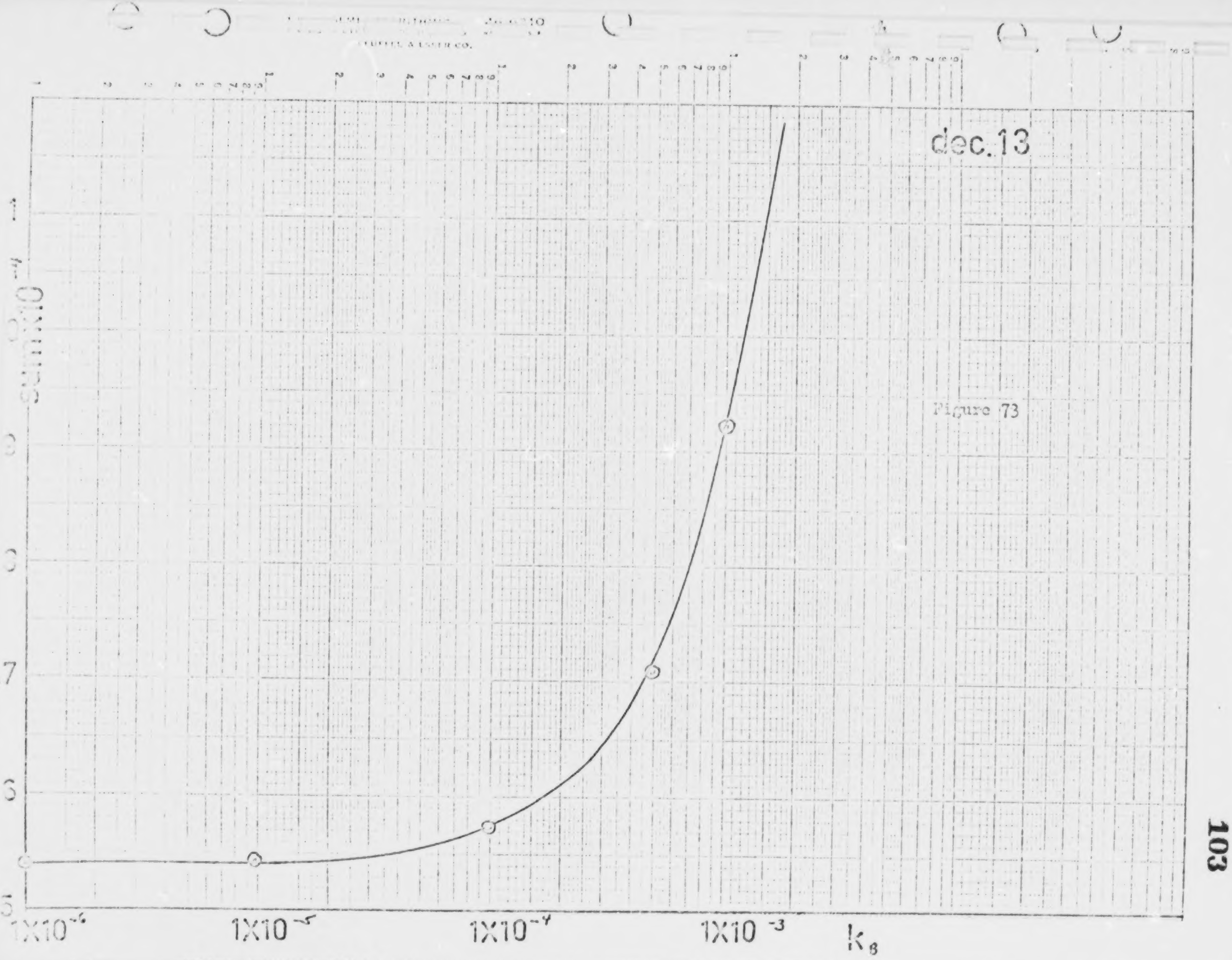
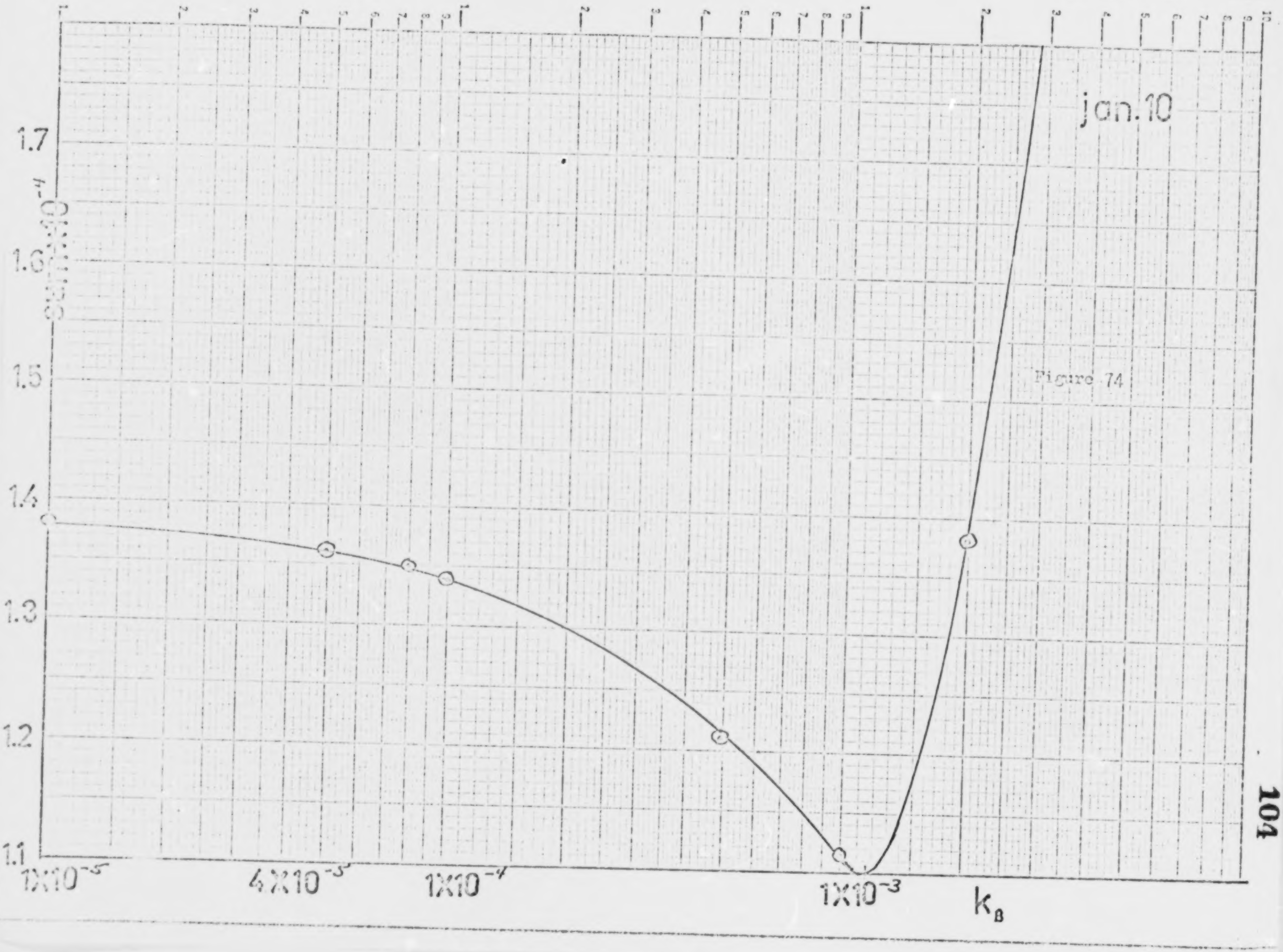


Figure 73


jan.10
Figure 74
OHMS×10^{-4}
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1×10^{-5}
4×10^{-5}
1×10^{-4}
1×10^{-3}
k_B

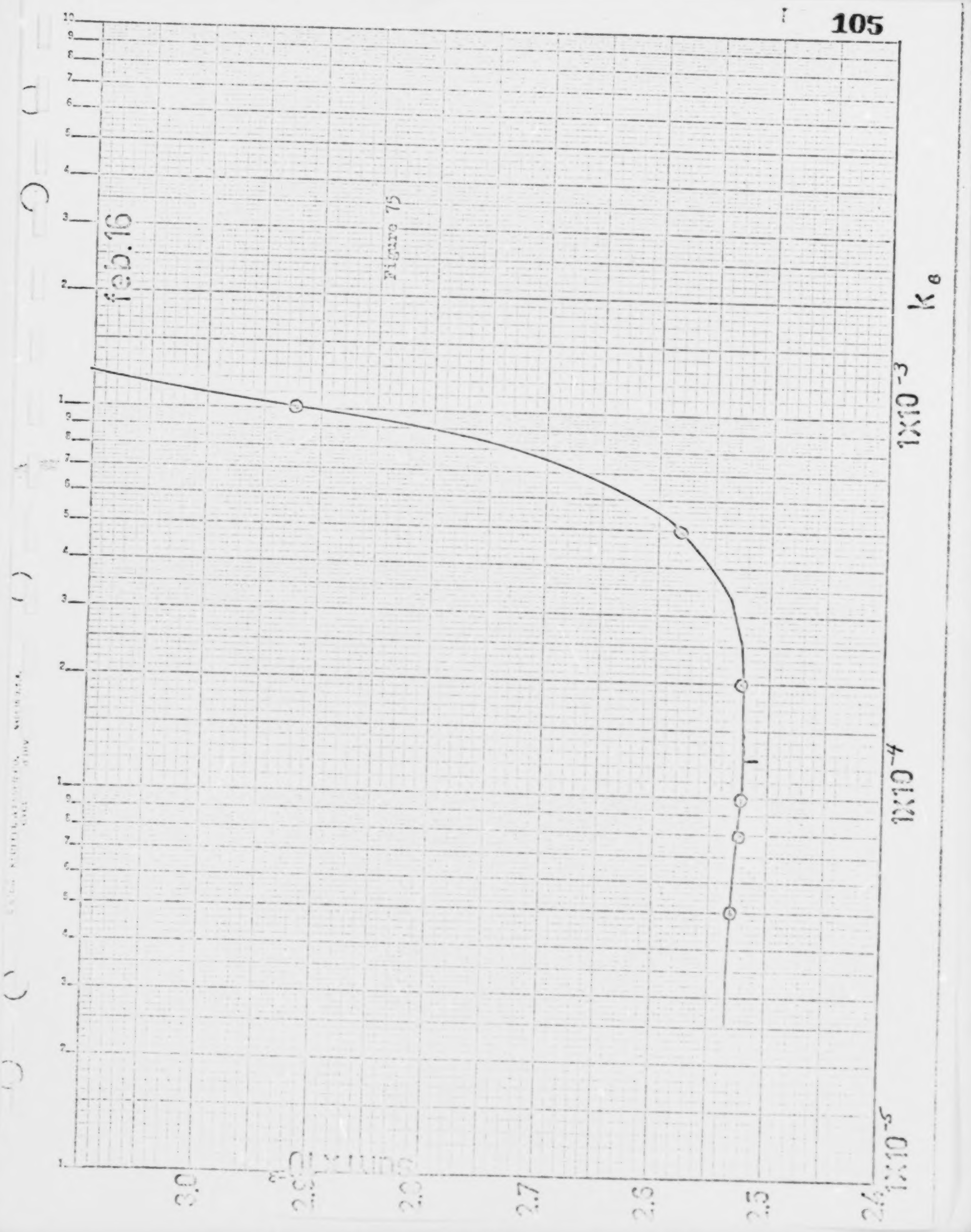
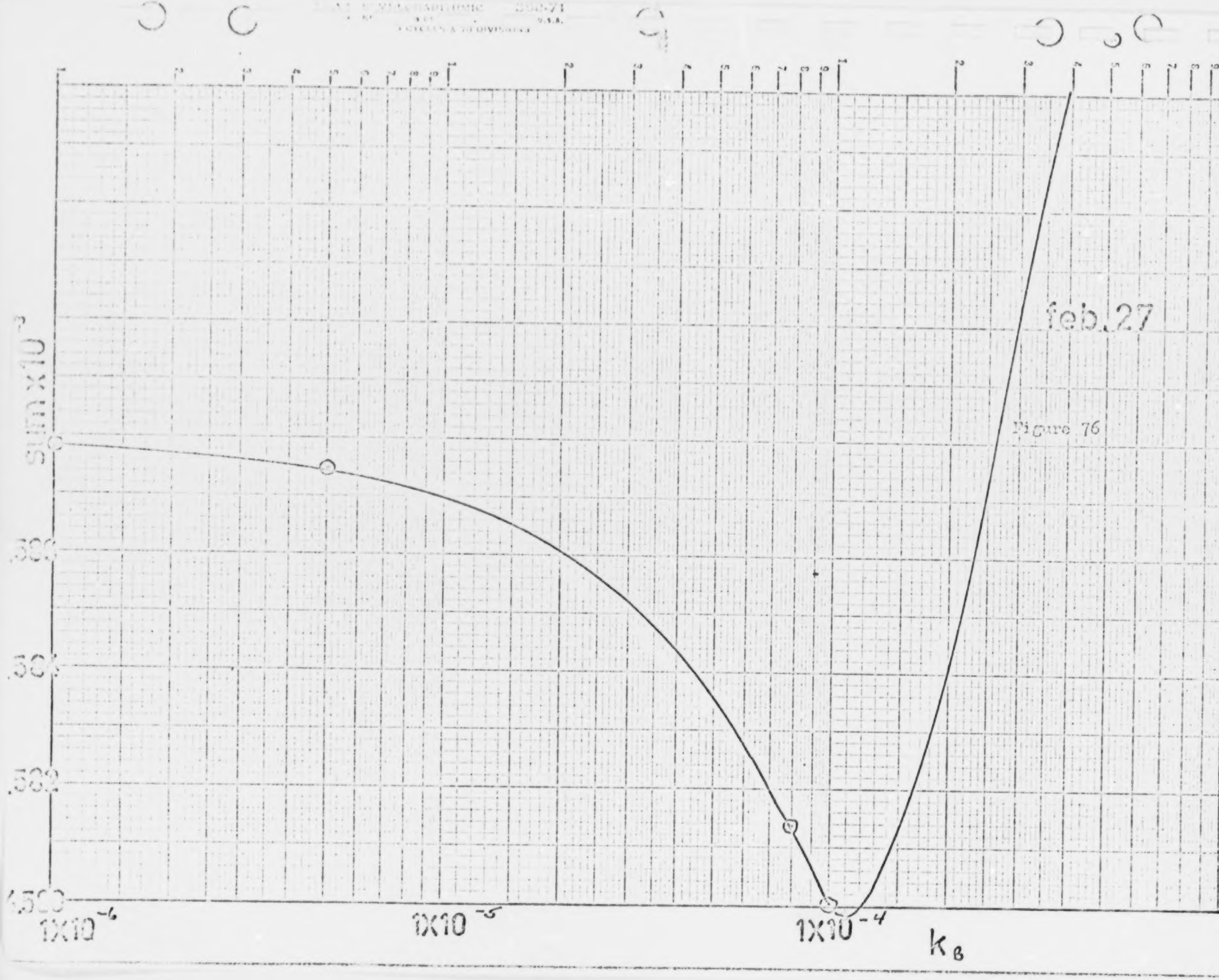


Figure 75


feb.27
Figure 76
sum x10^-3
.506
.504
.502
.4500
1X10^-6
1X10^-5
1X10^-4
k_B

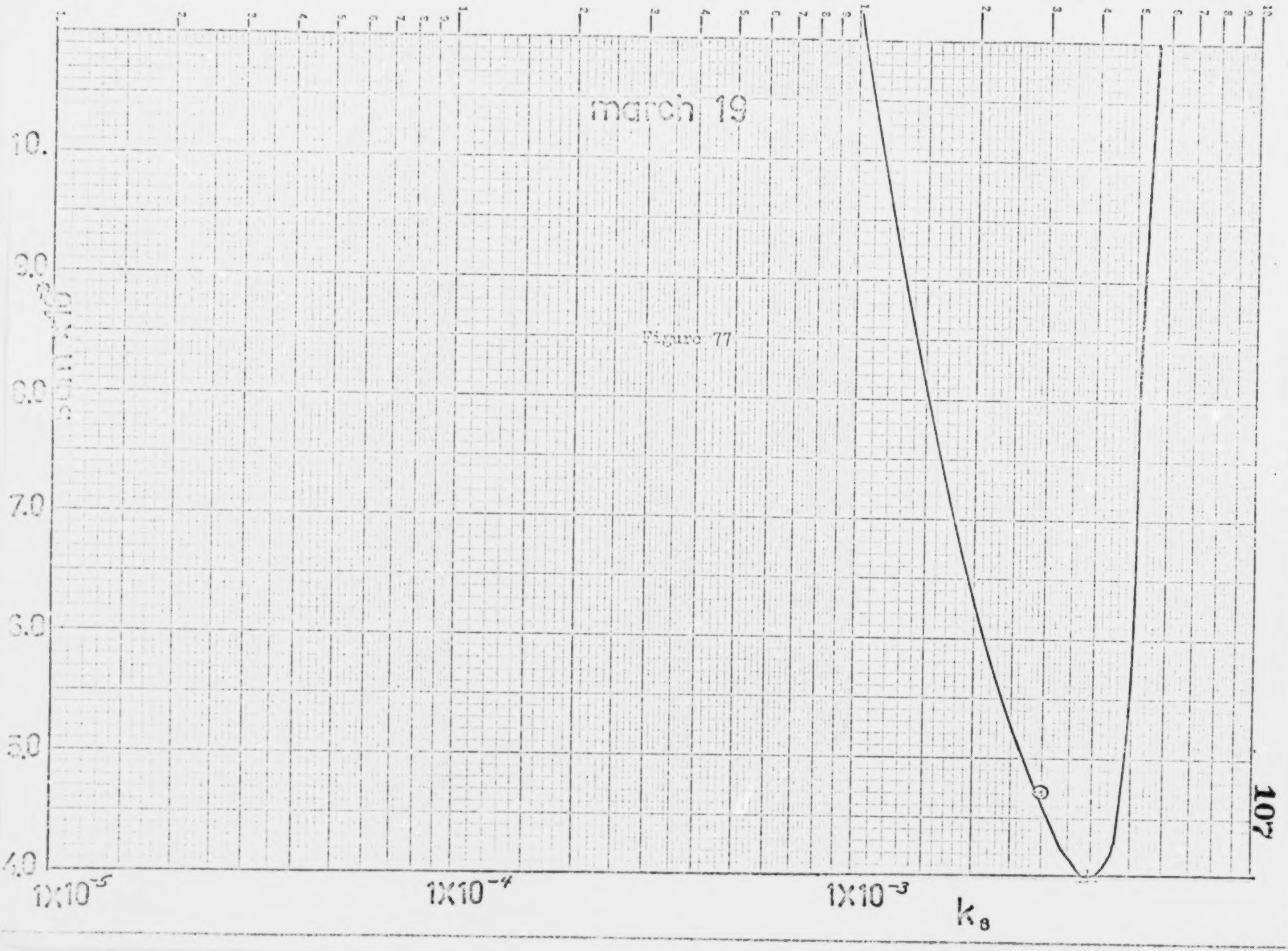
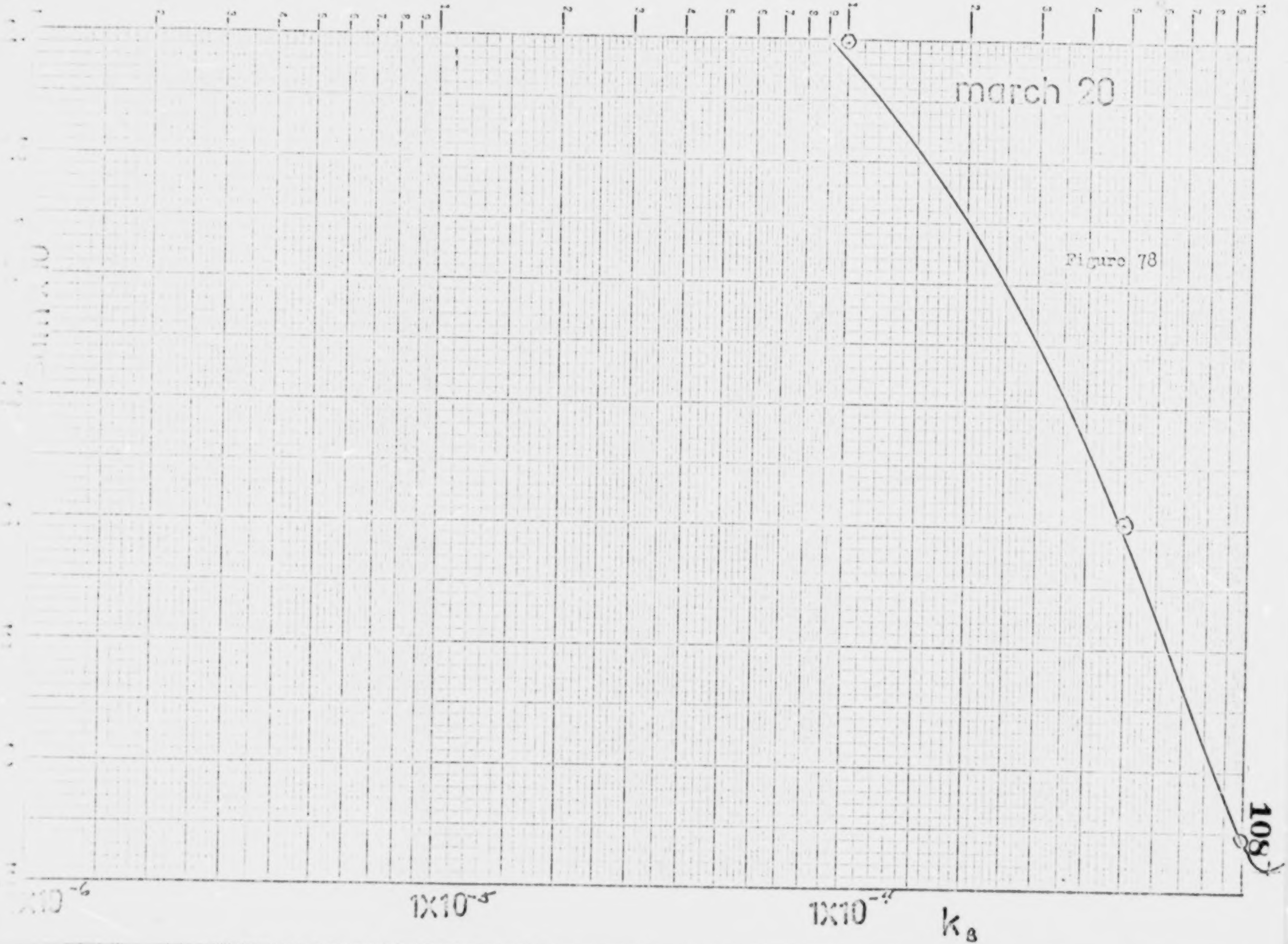


Figure 77


march 20
Figure 78
1X10^-6
1X10^-5
1X10^-4
k_s

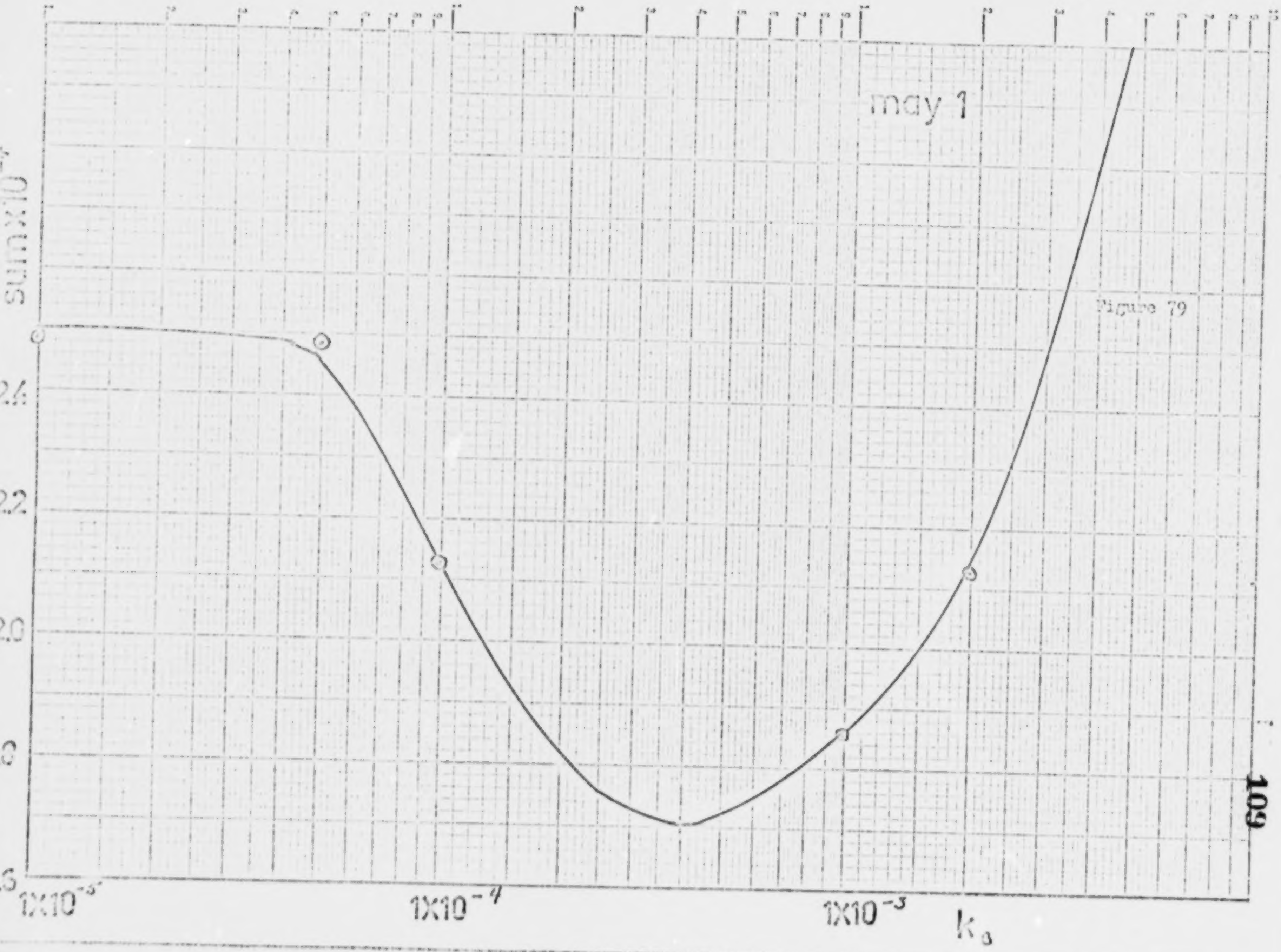


Figure 79

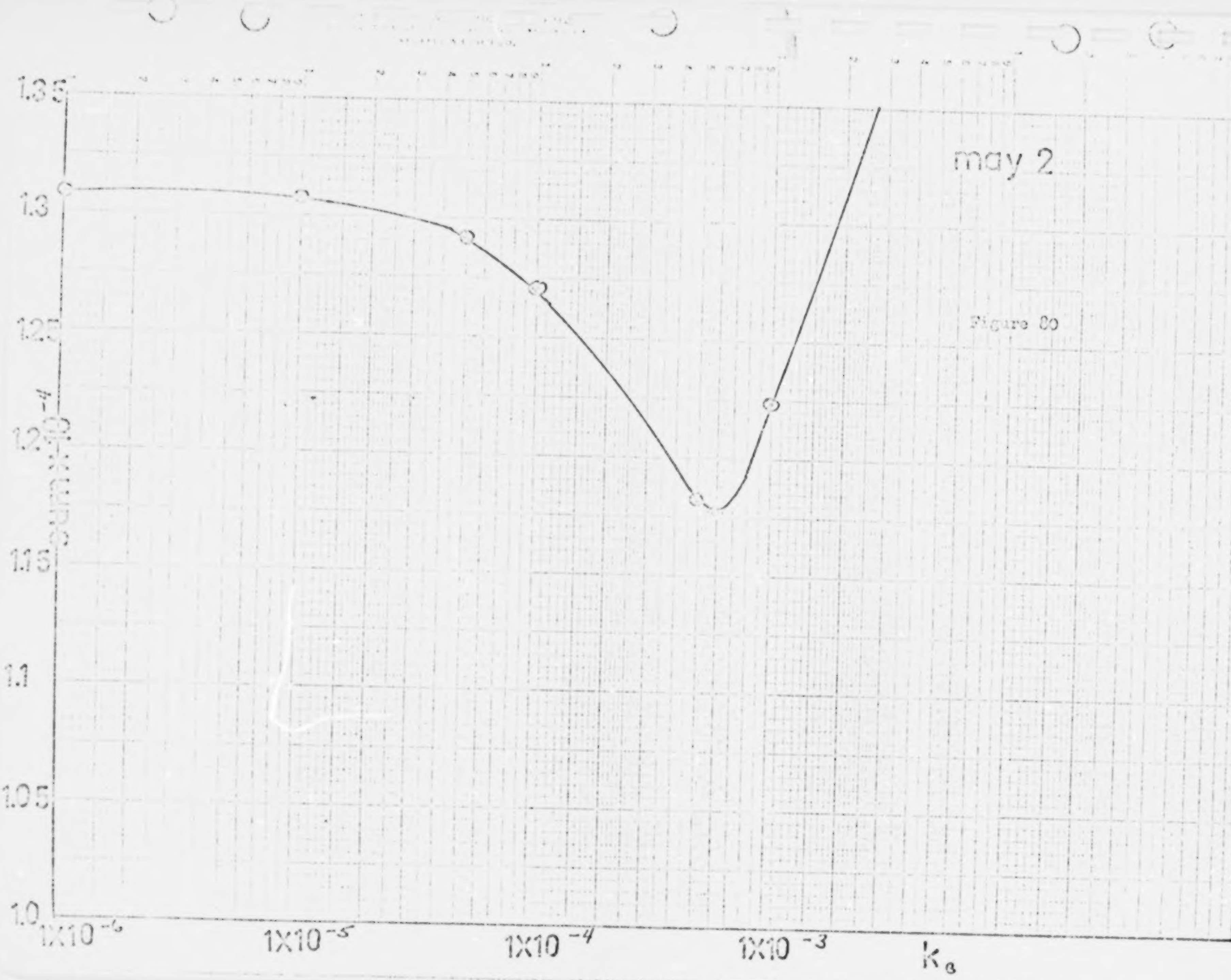


Figure 80

may 2
Sm x 10^{-4}
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1.0
1X10^{-6}
1X10^{-5}
1X10^{-4}
1X10^{-3}
K_a

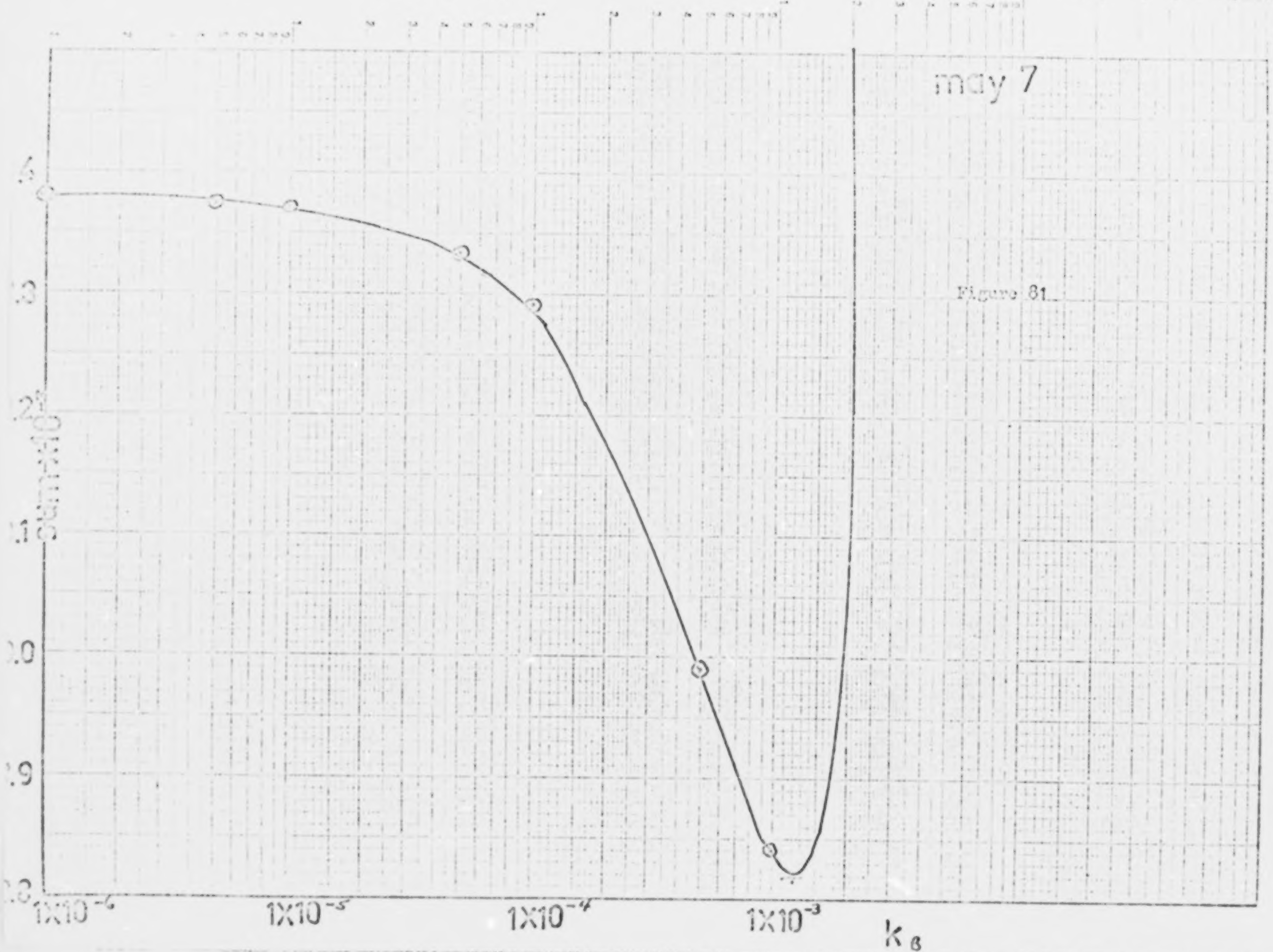


Figure 81

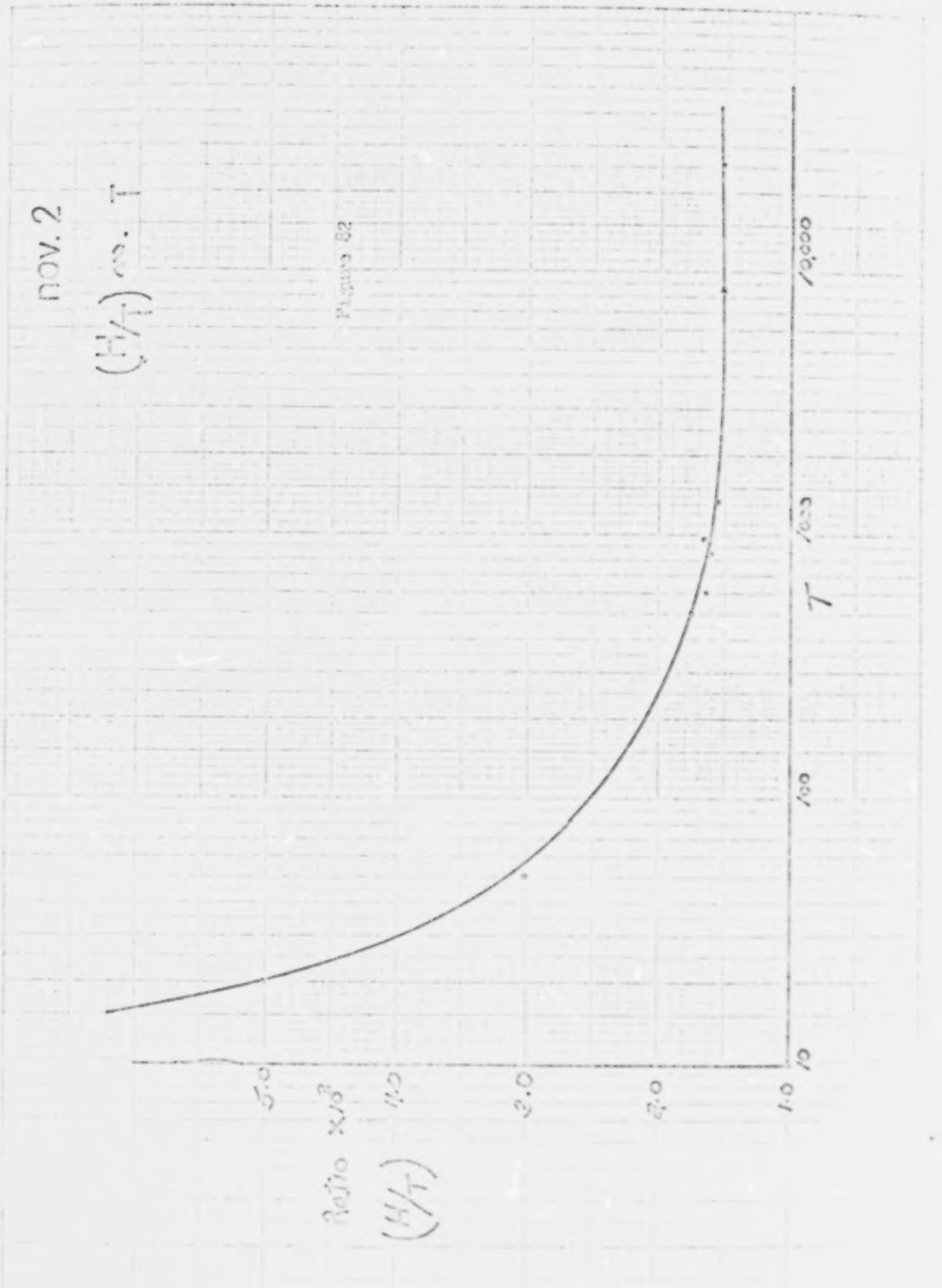


Figure 82

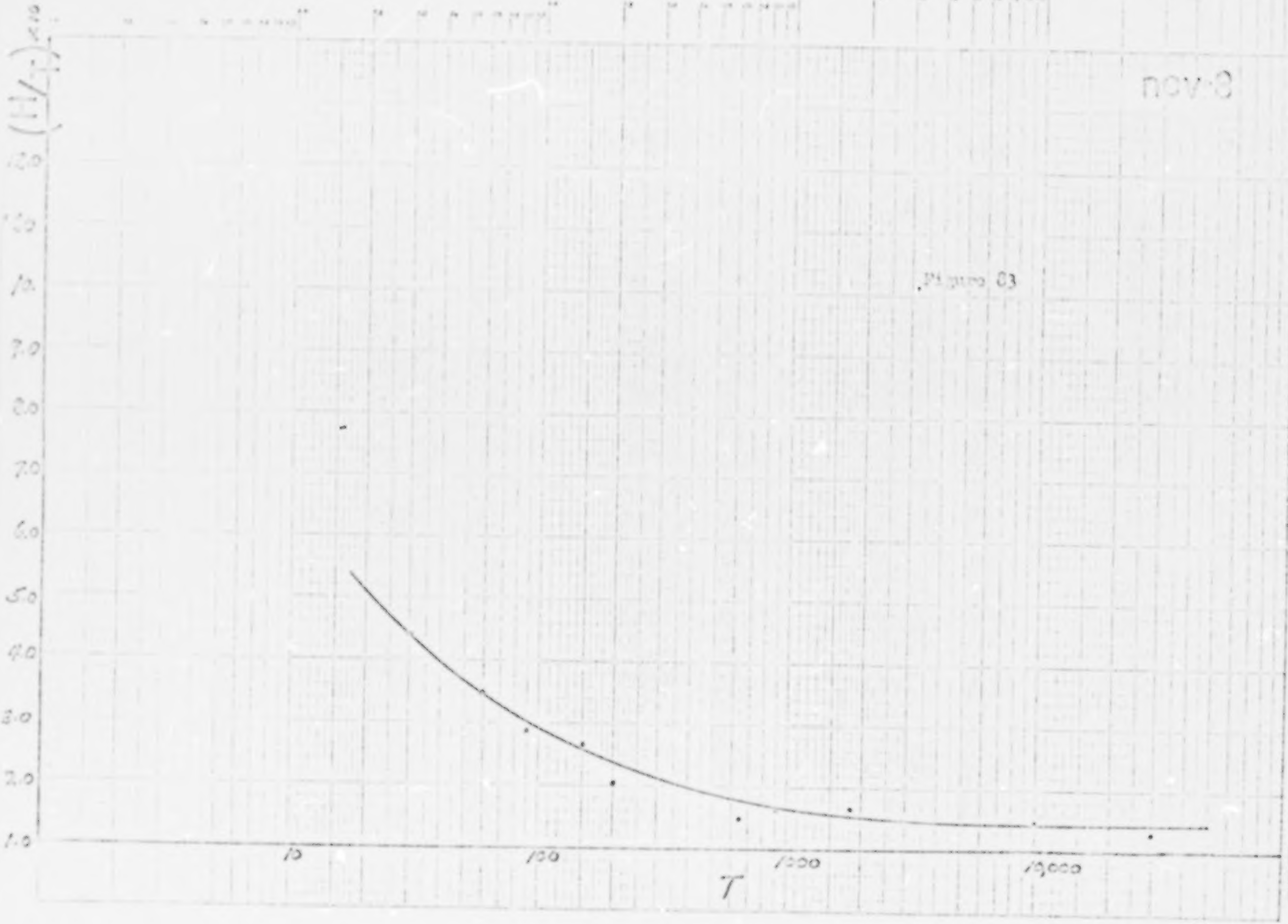


Figure 83

nov·8
(H/H1) ×10
12.0
11.0
10.
9.0
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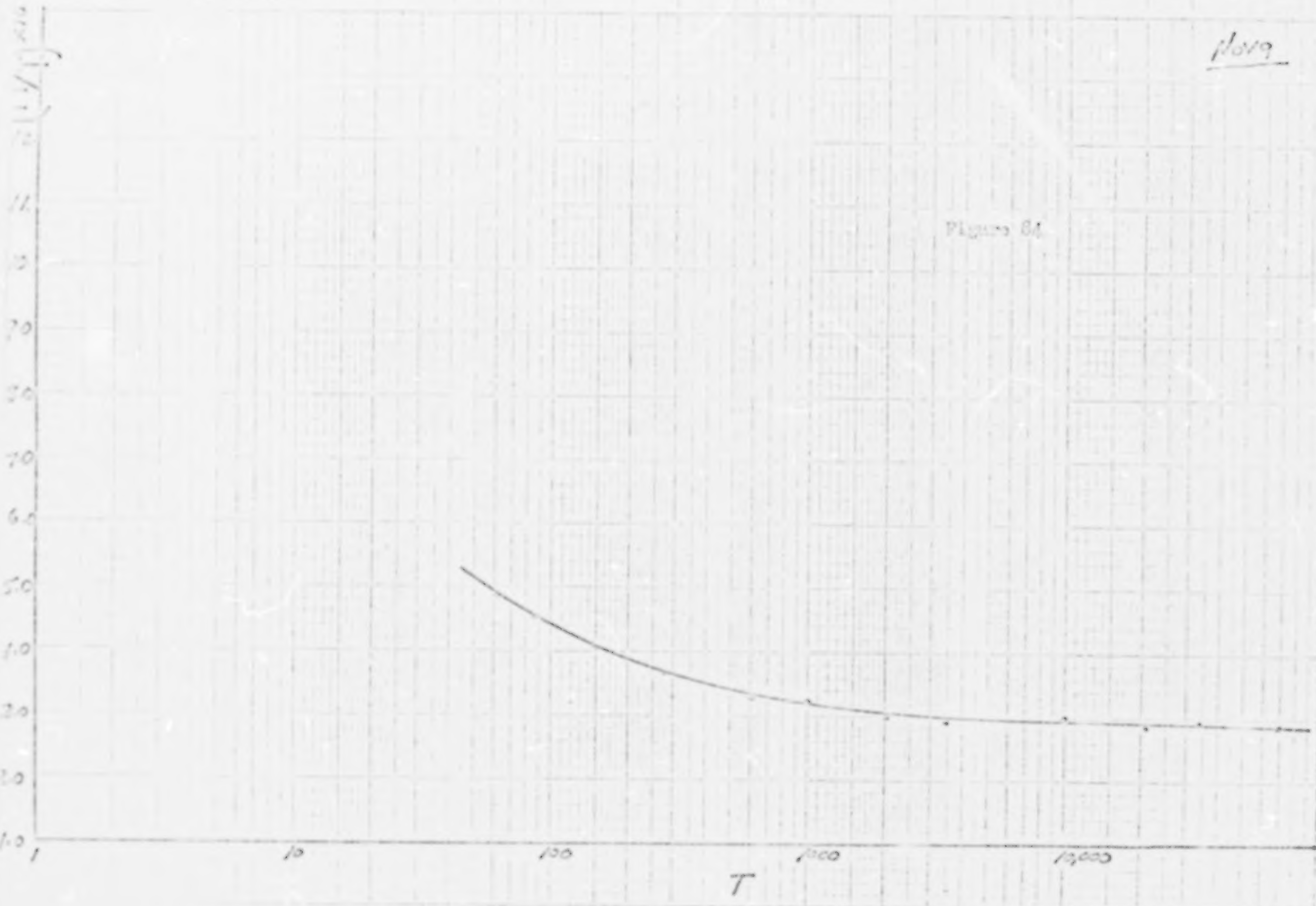

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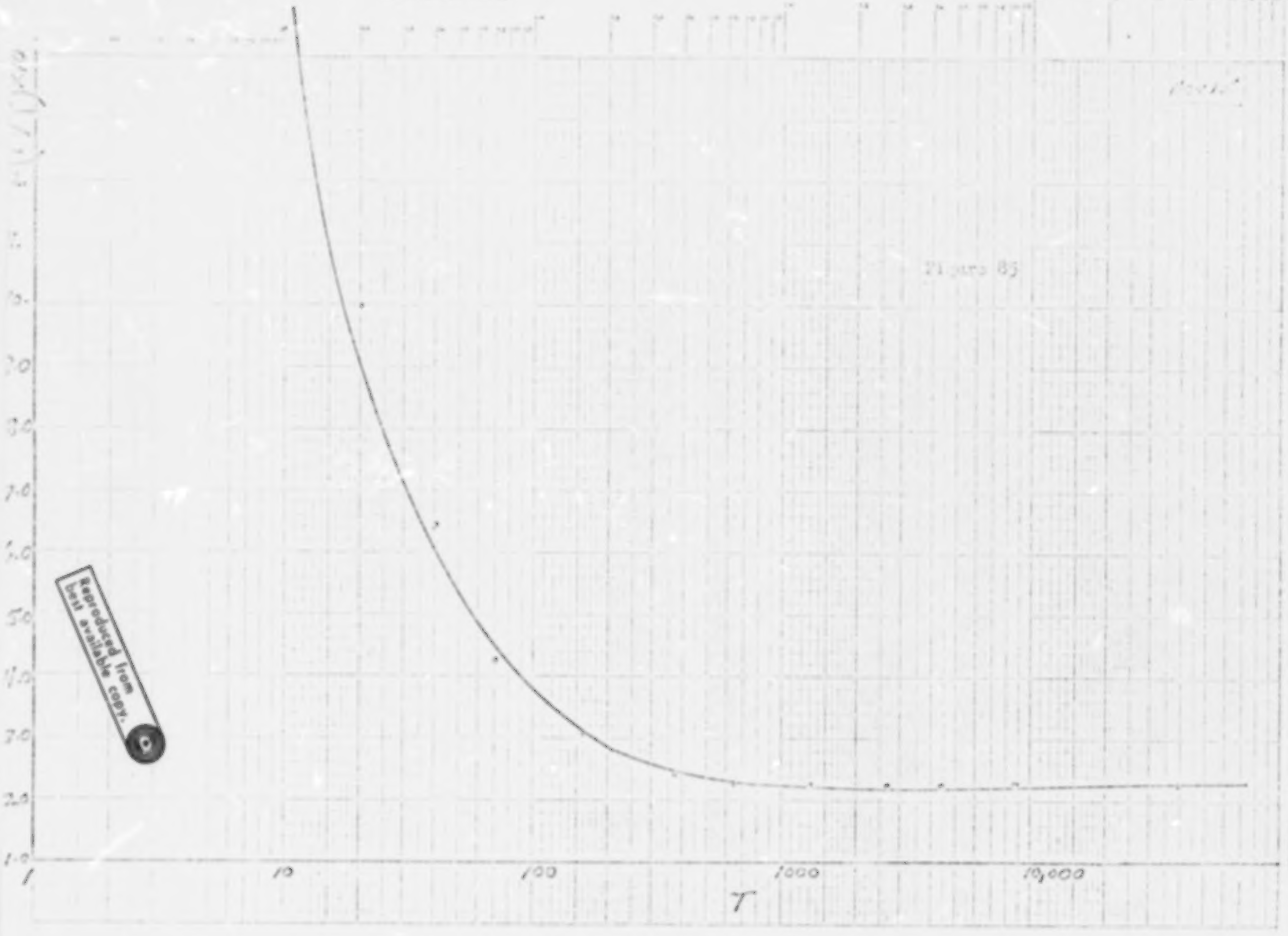

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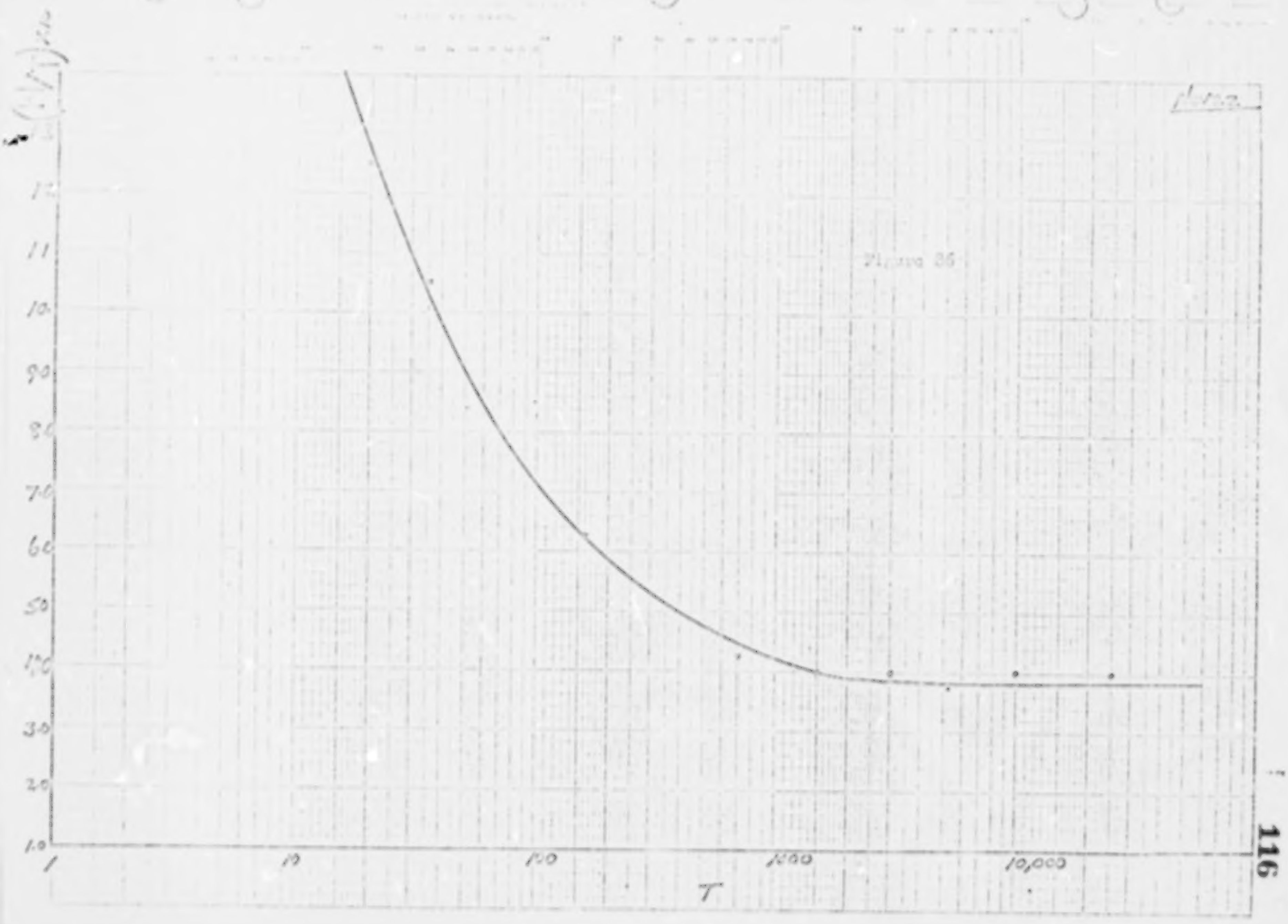

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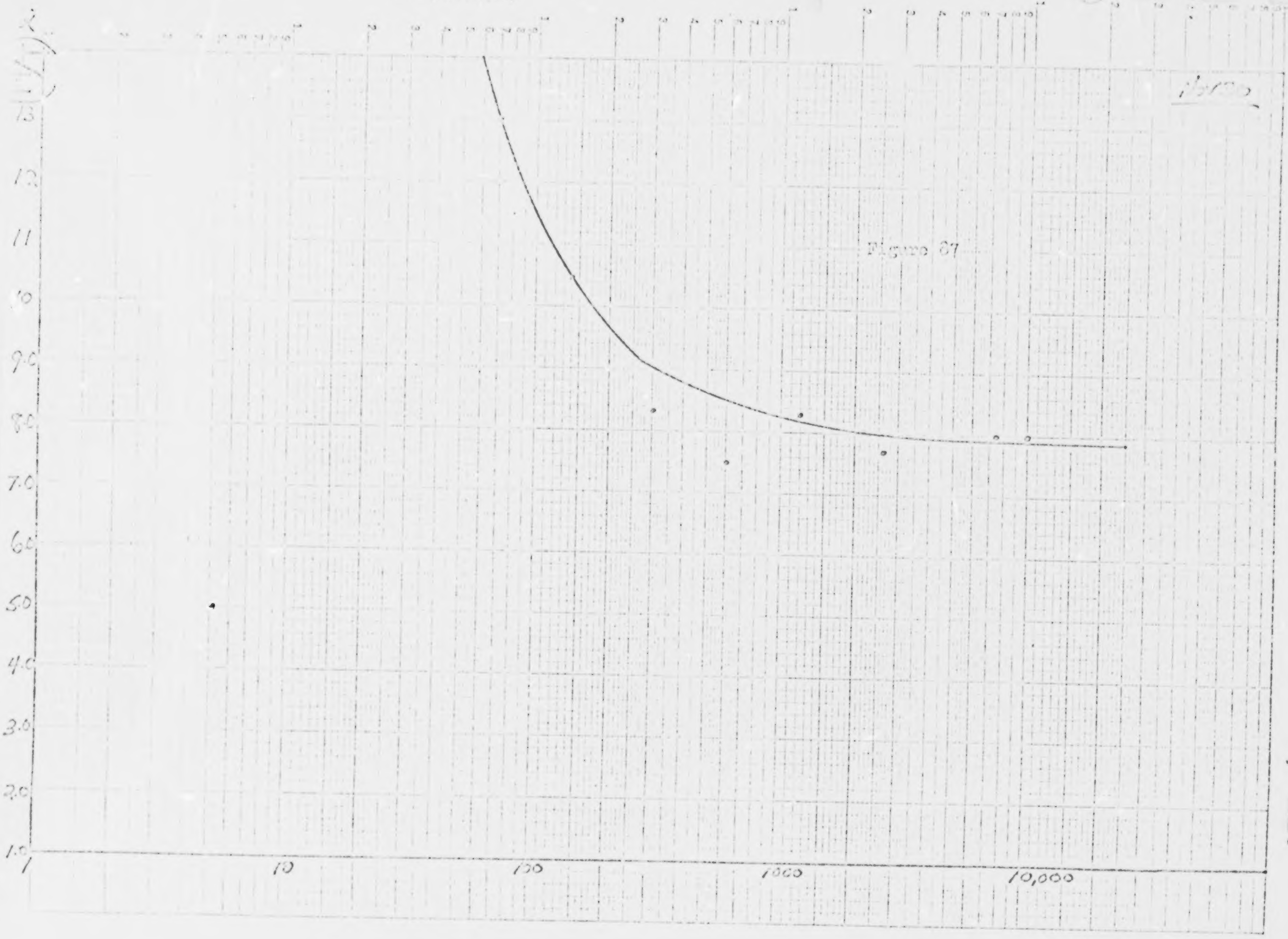
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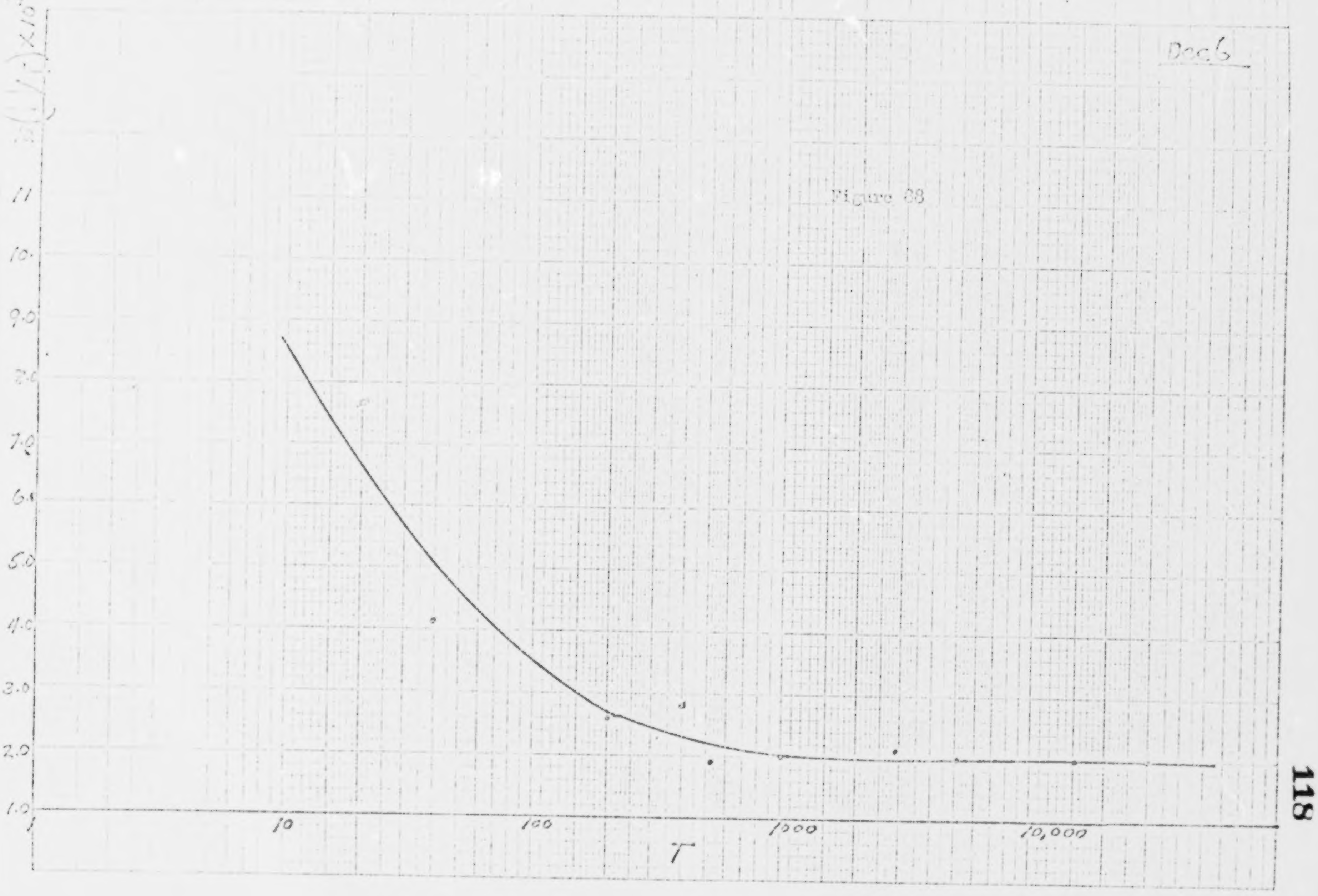

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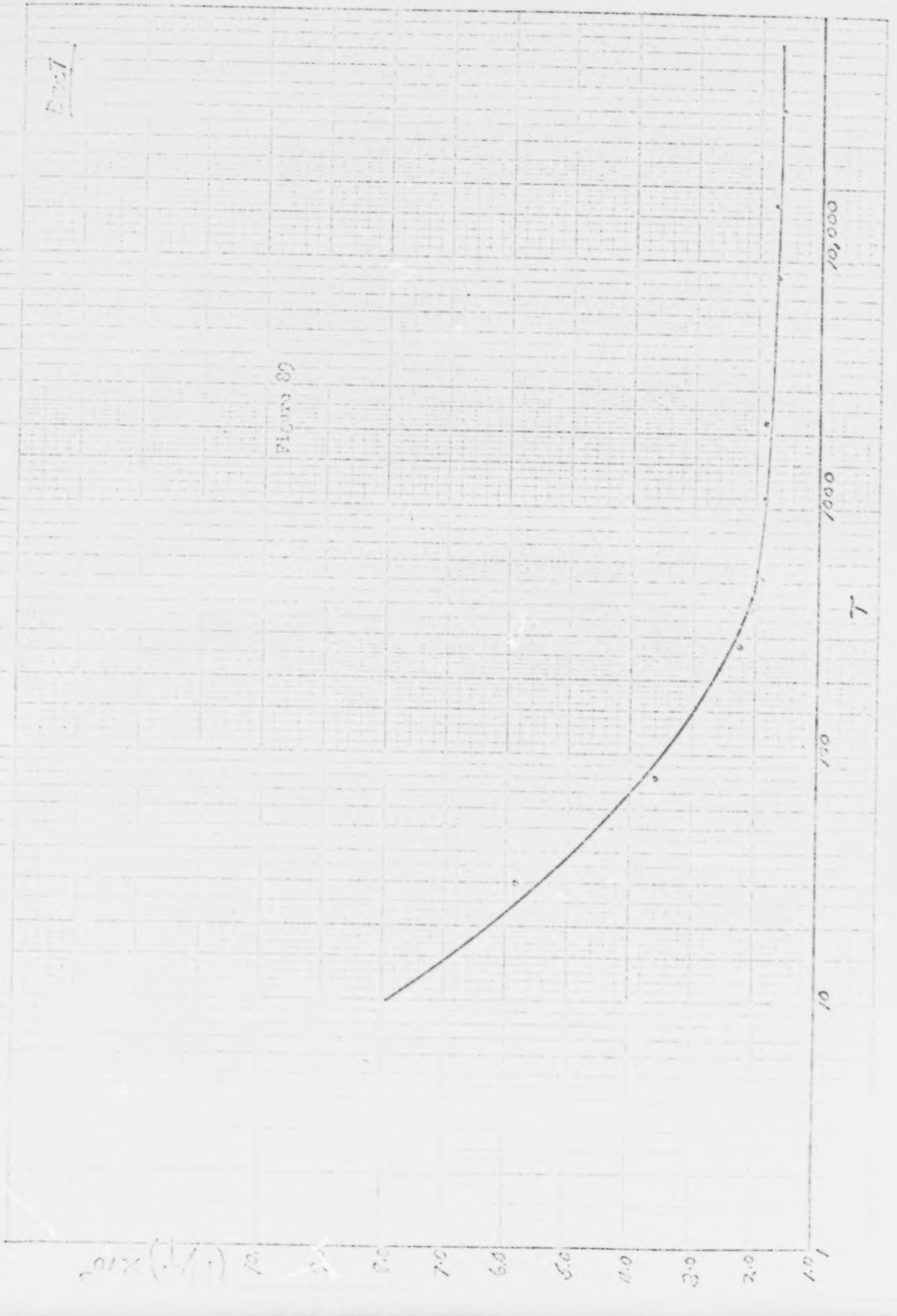

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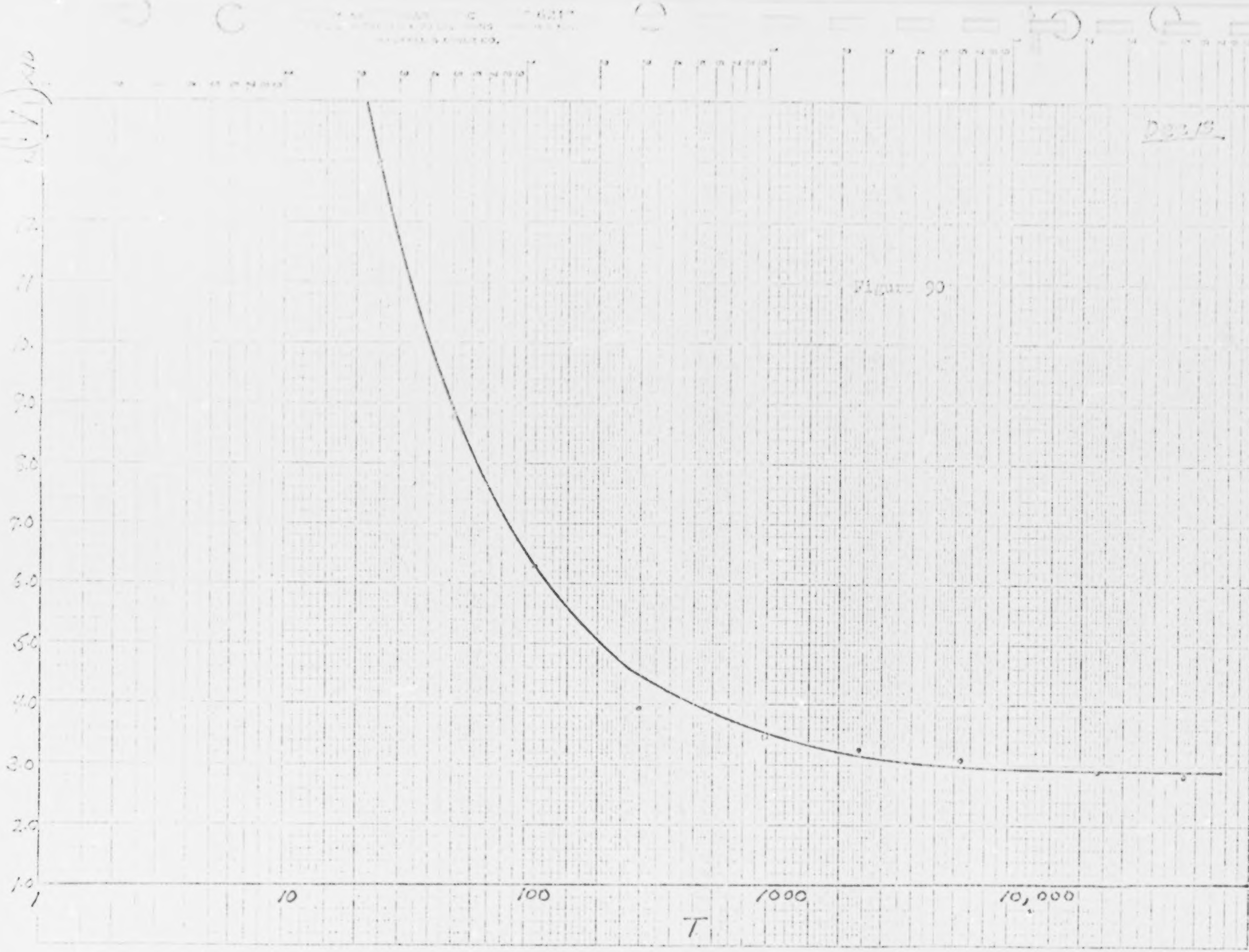

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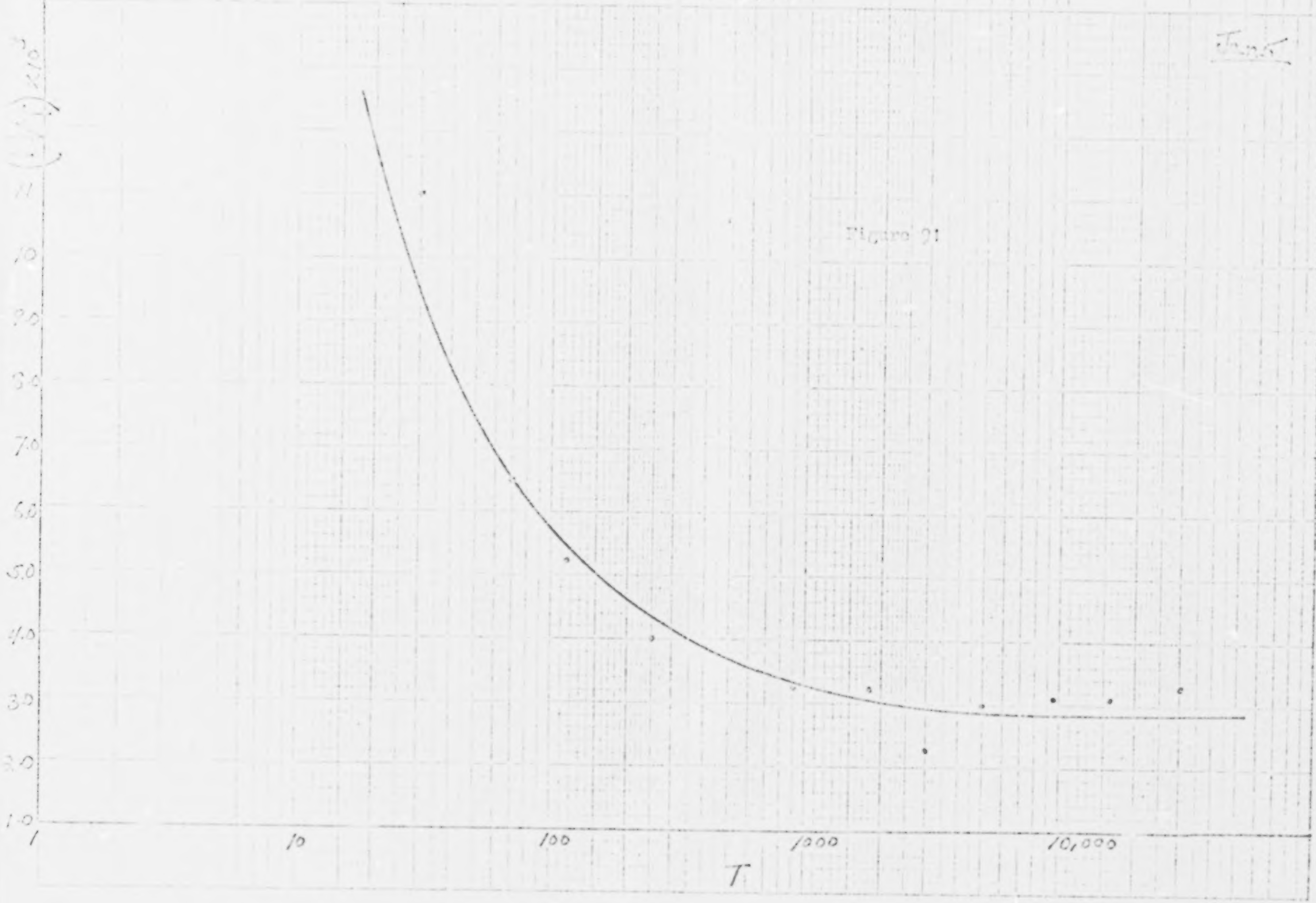

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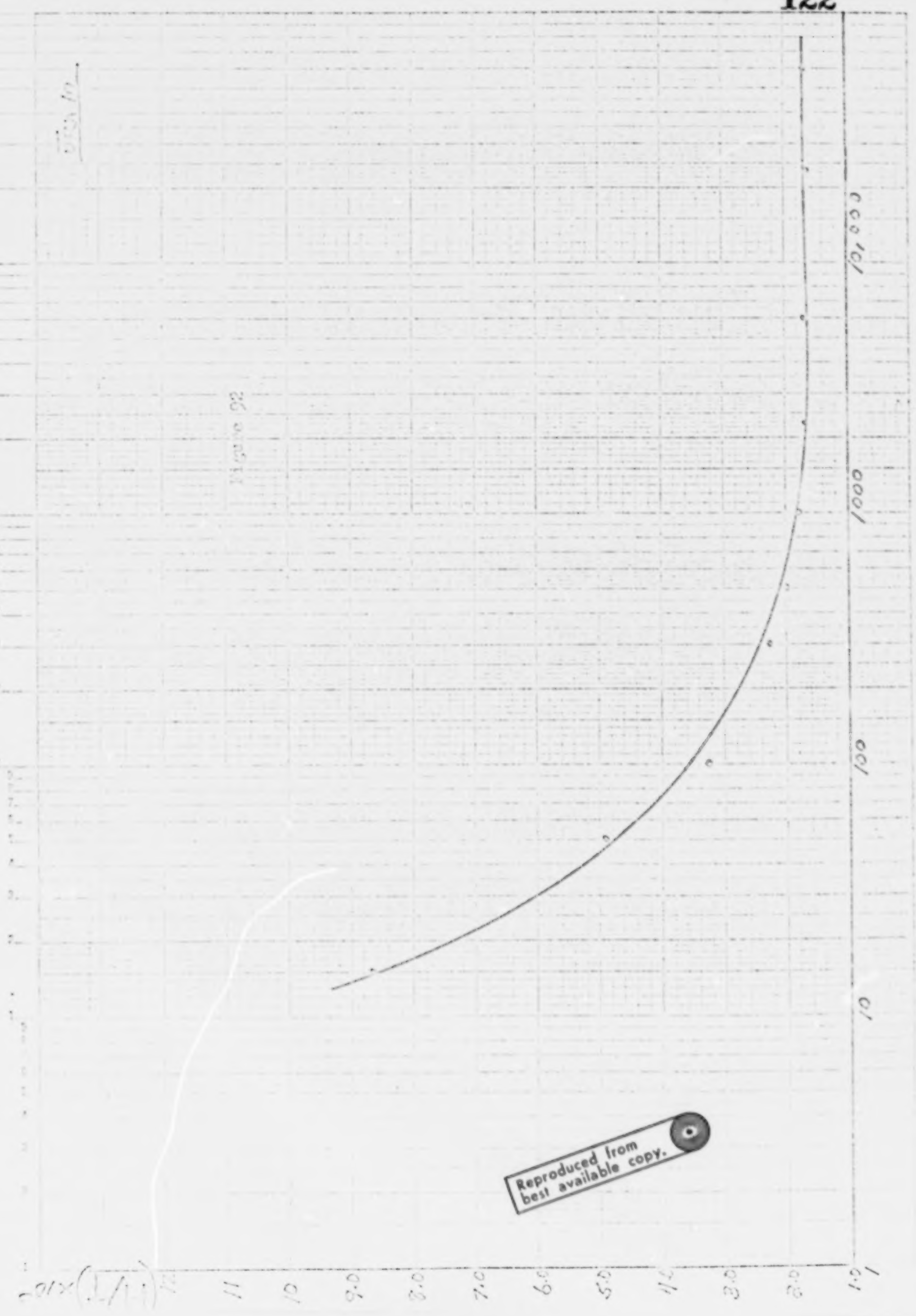

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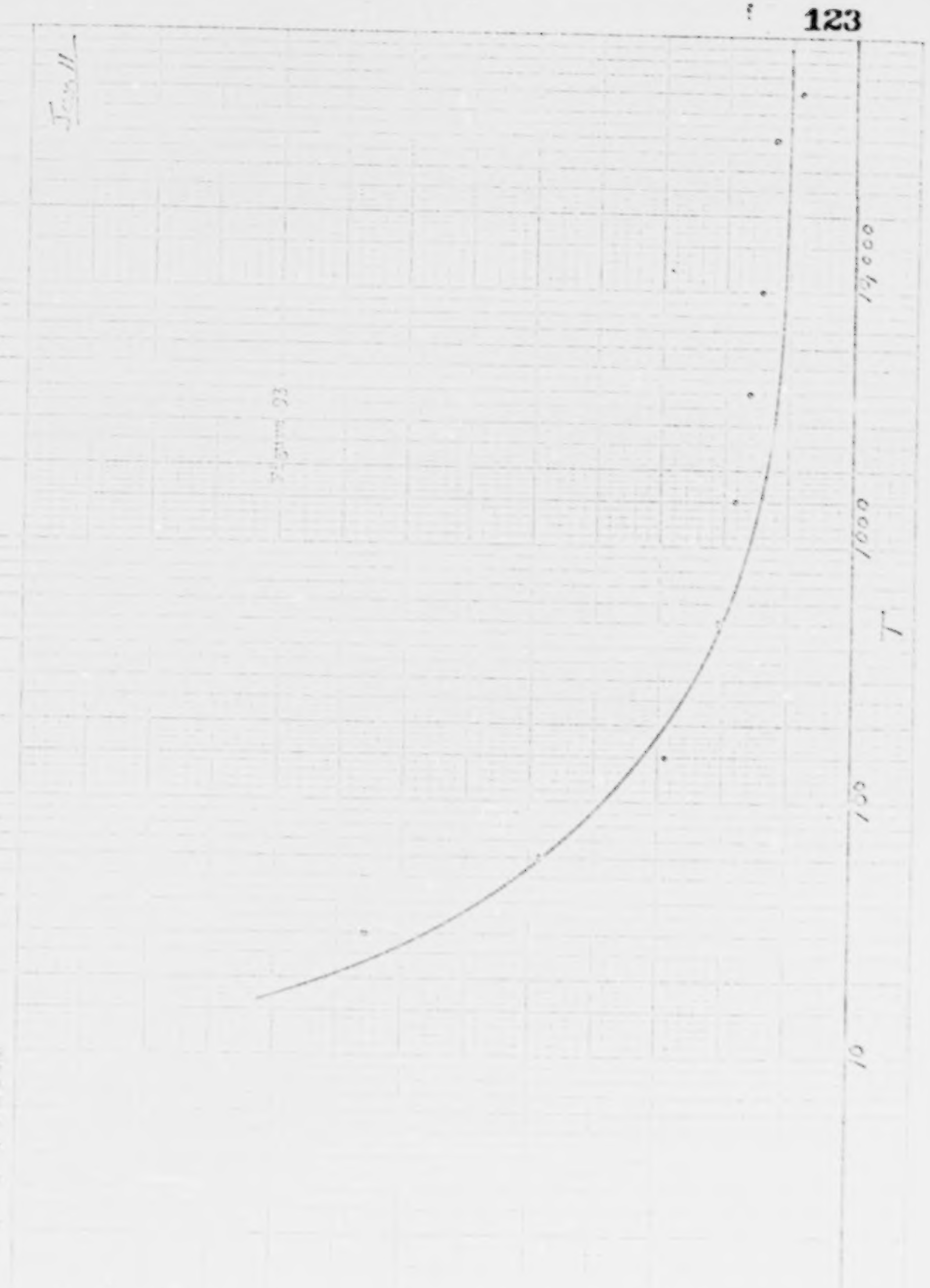
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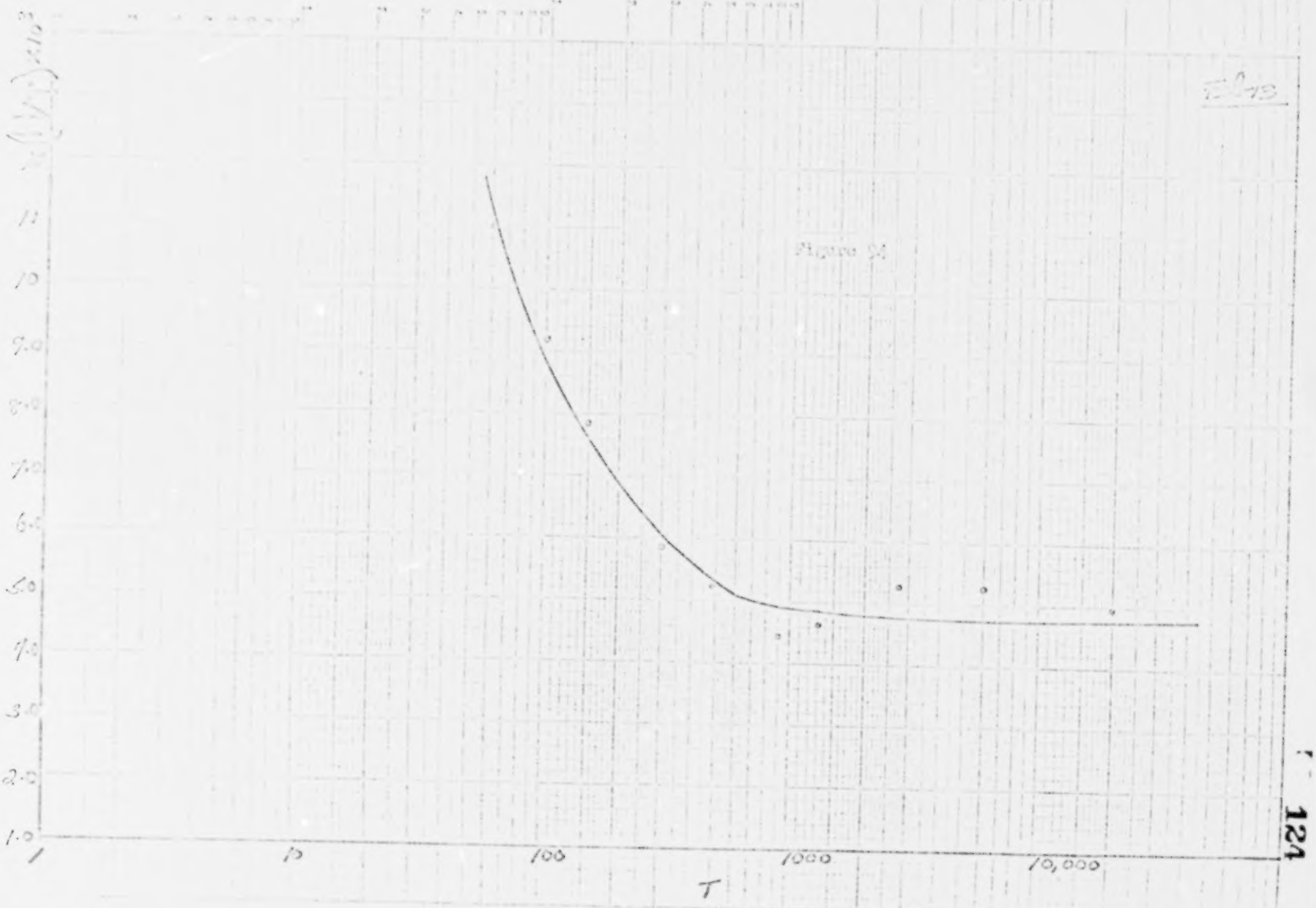
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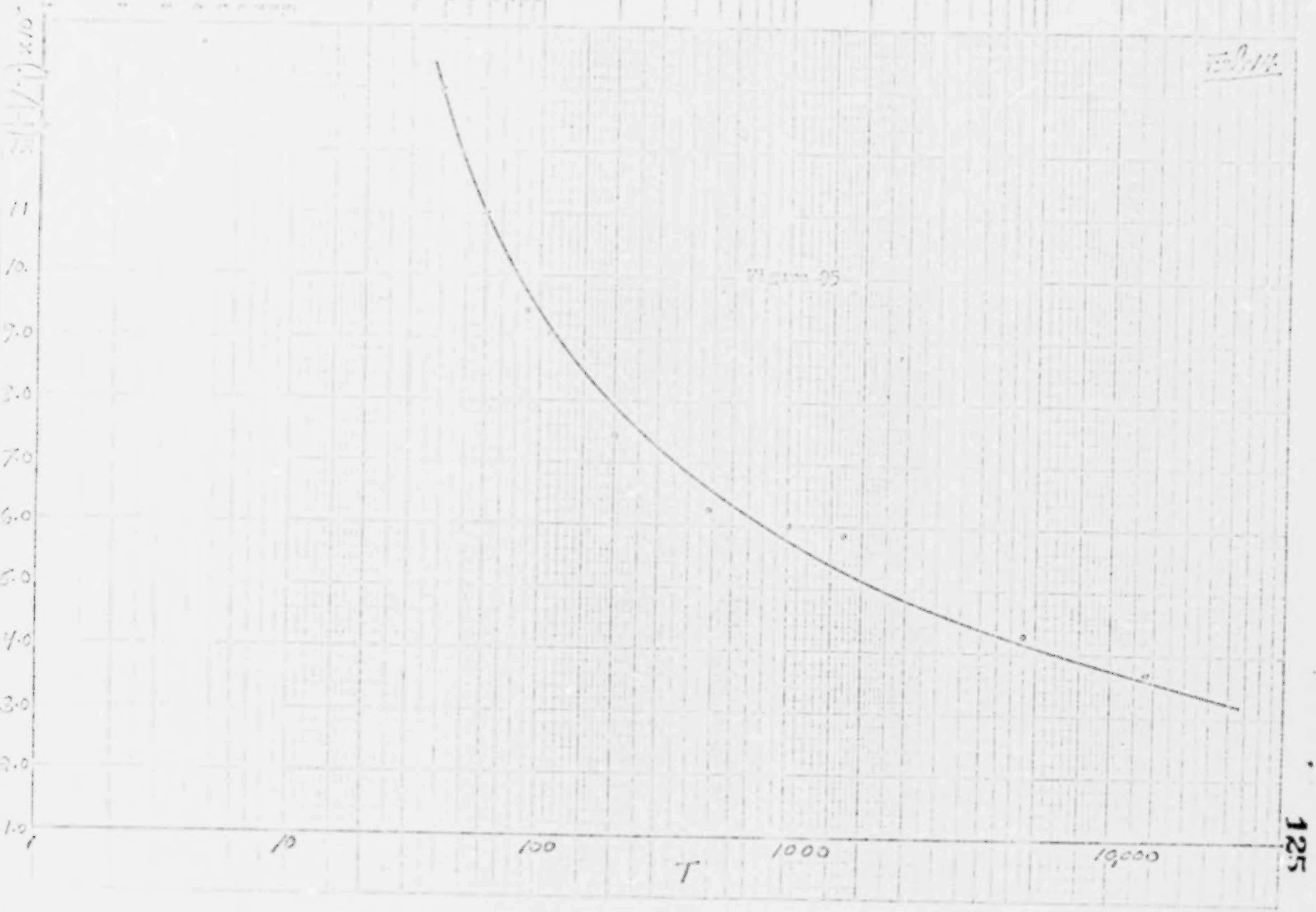

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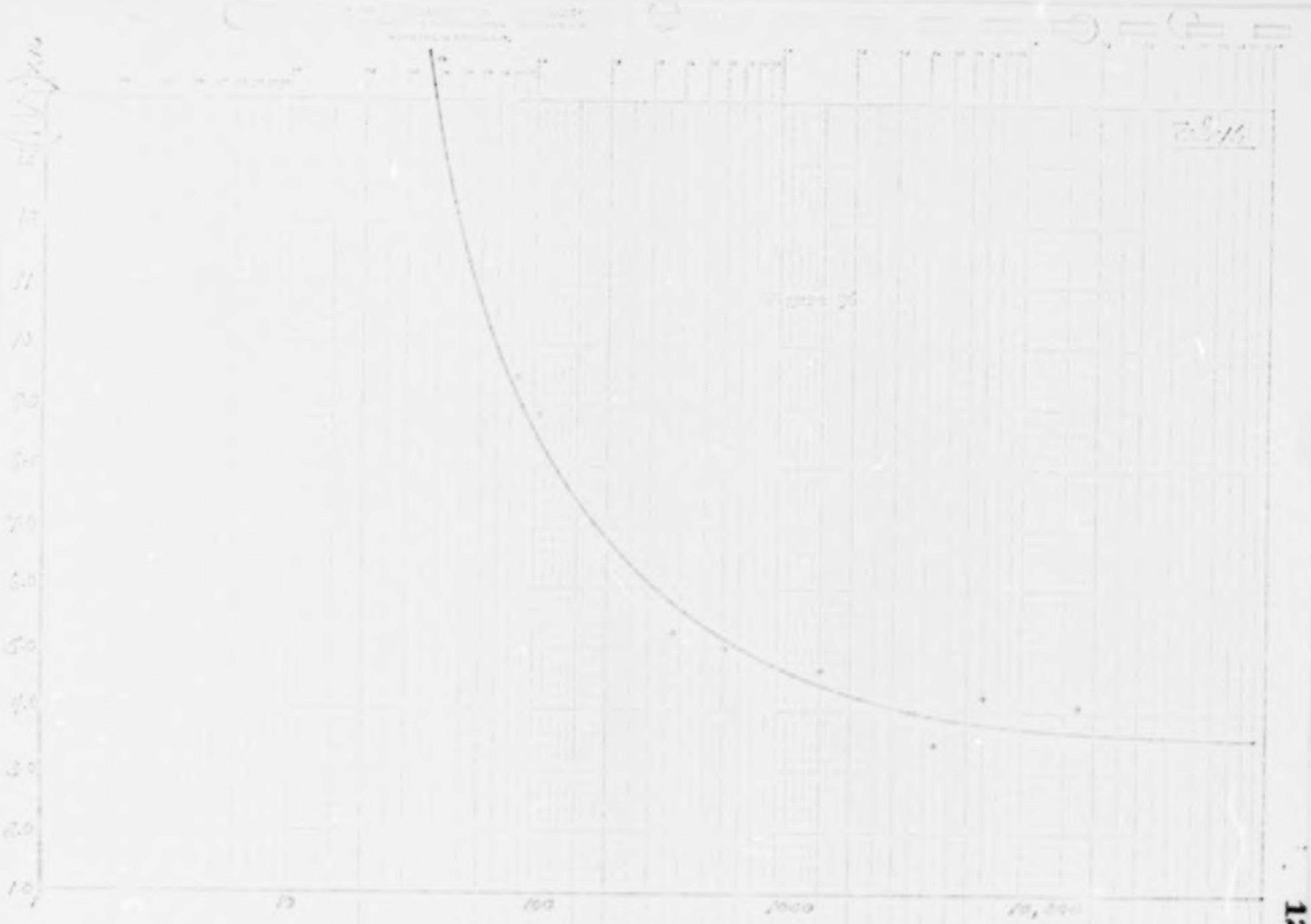
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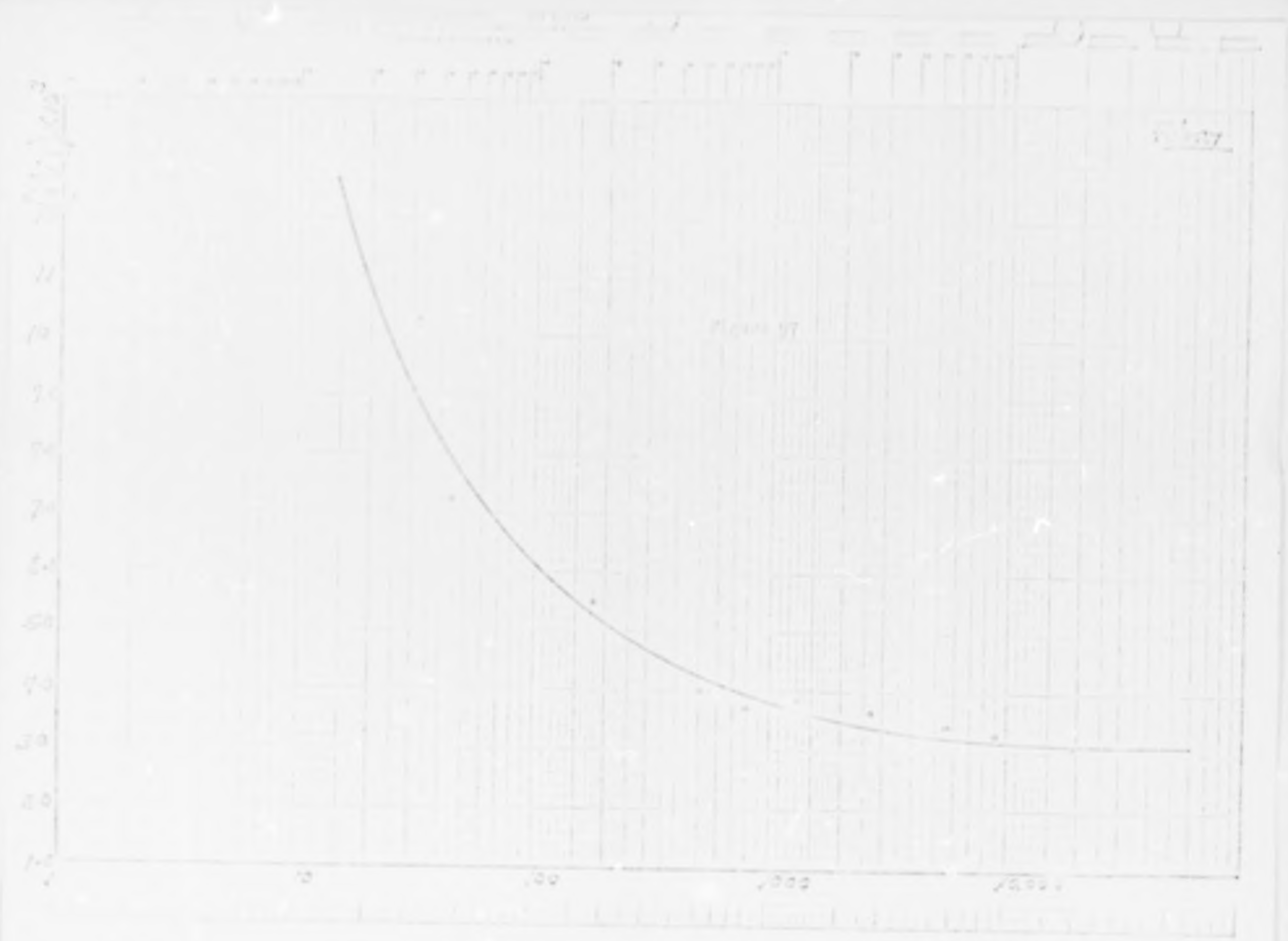Fig. 37
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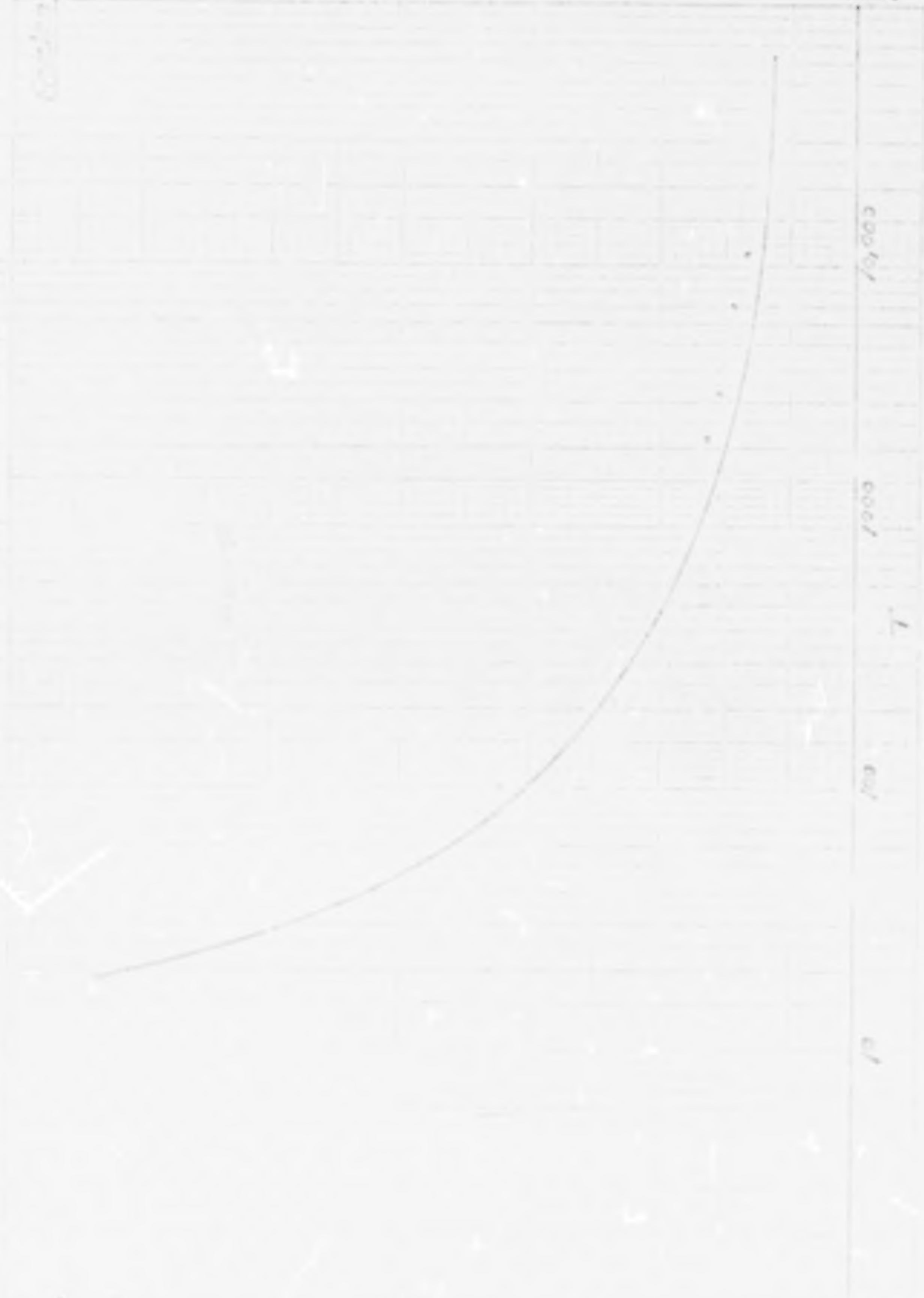
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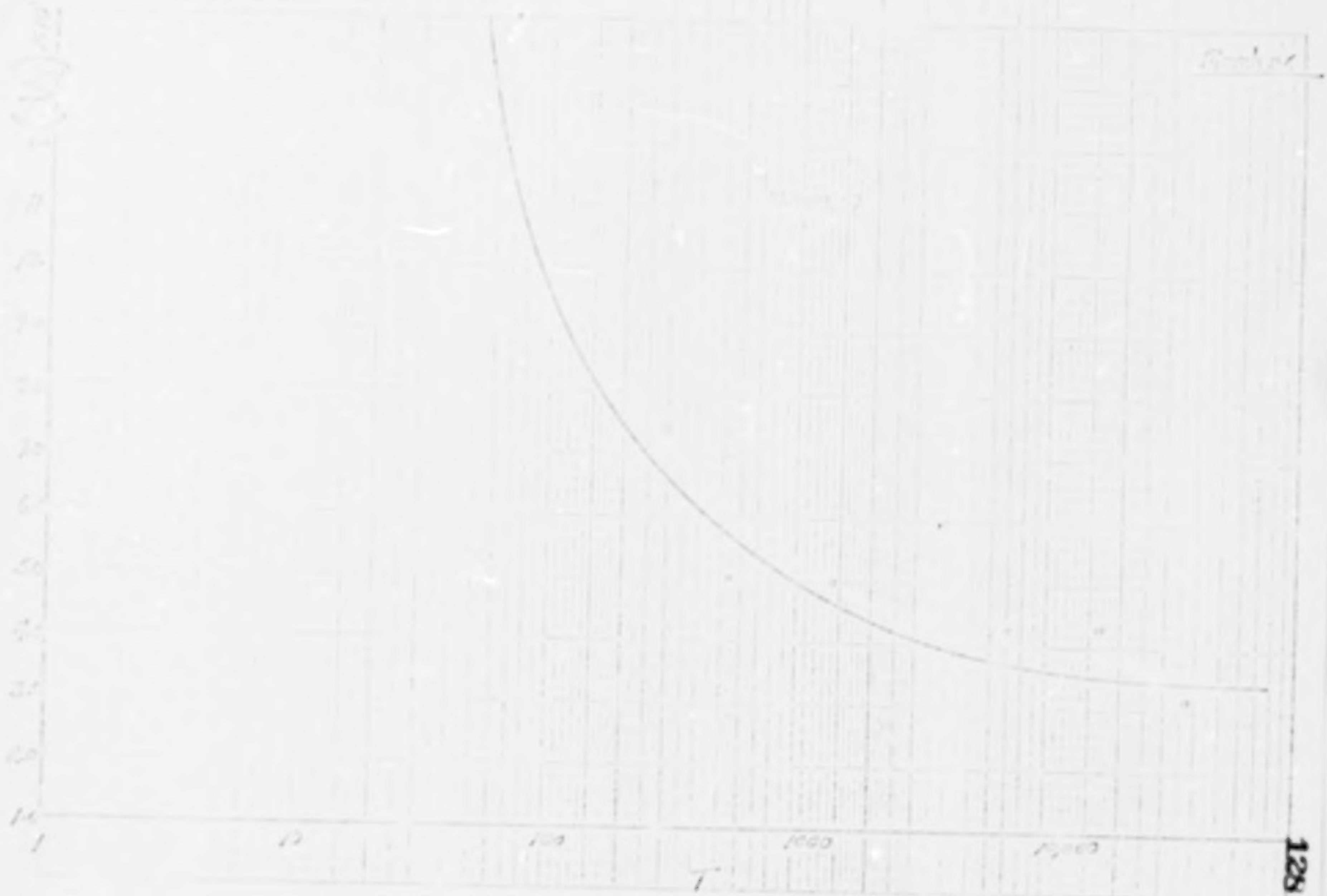
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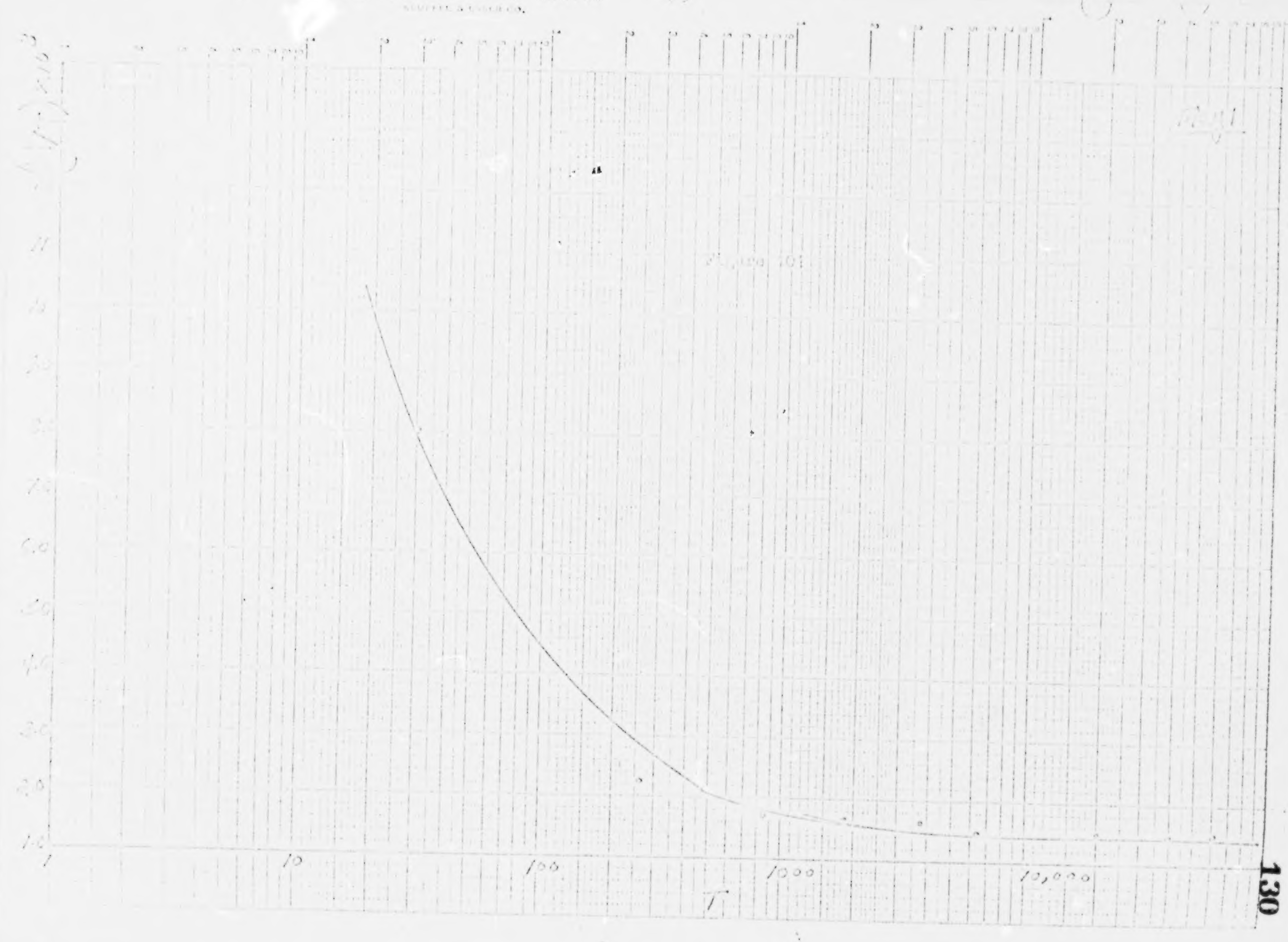
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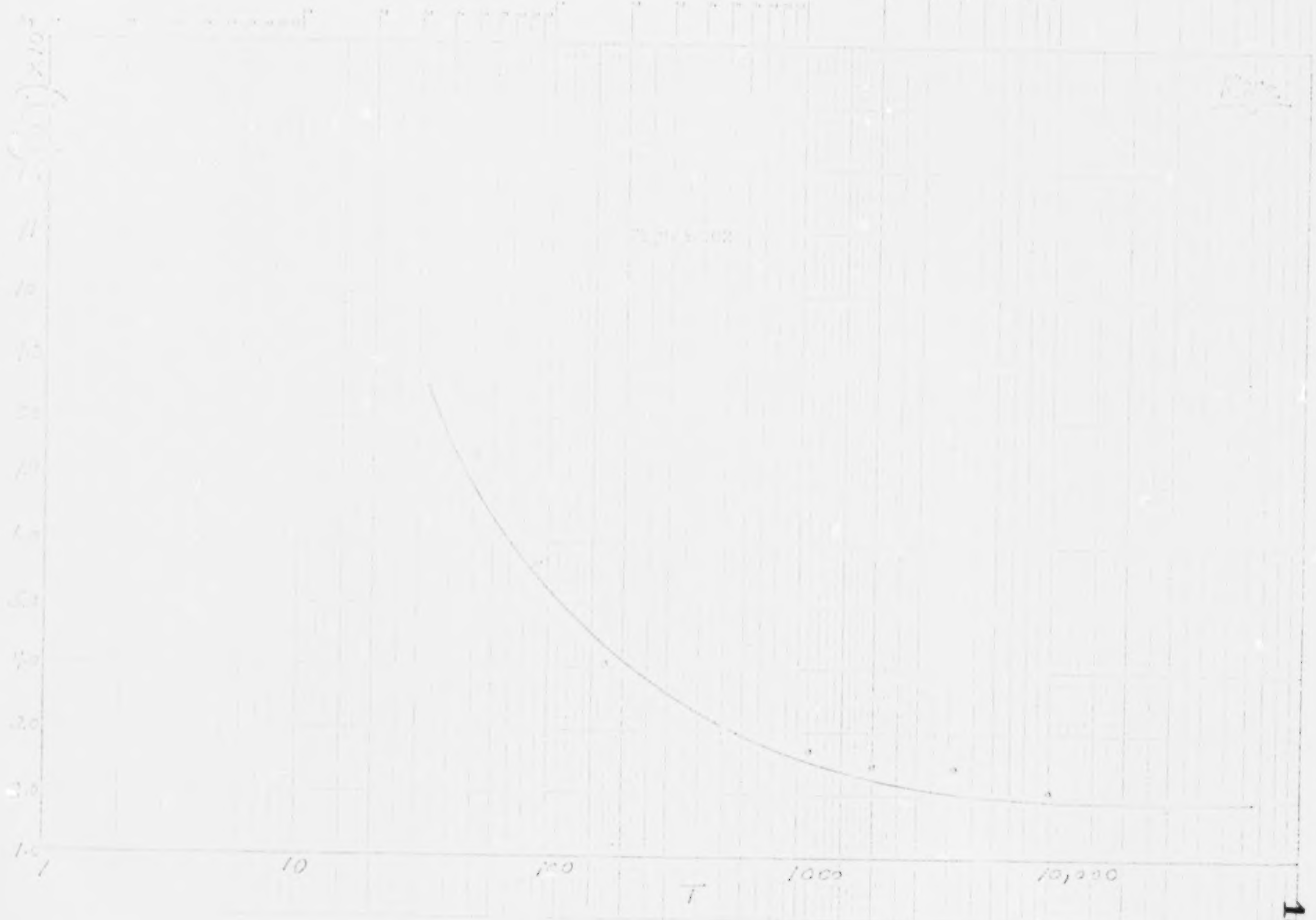
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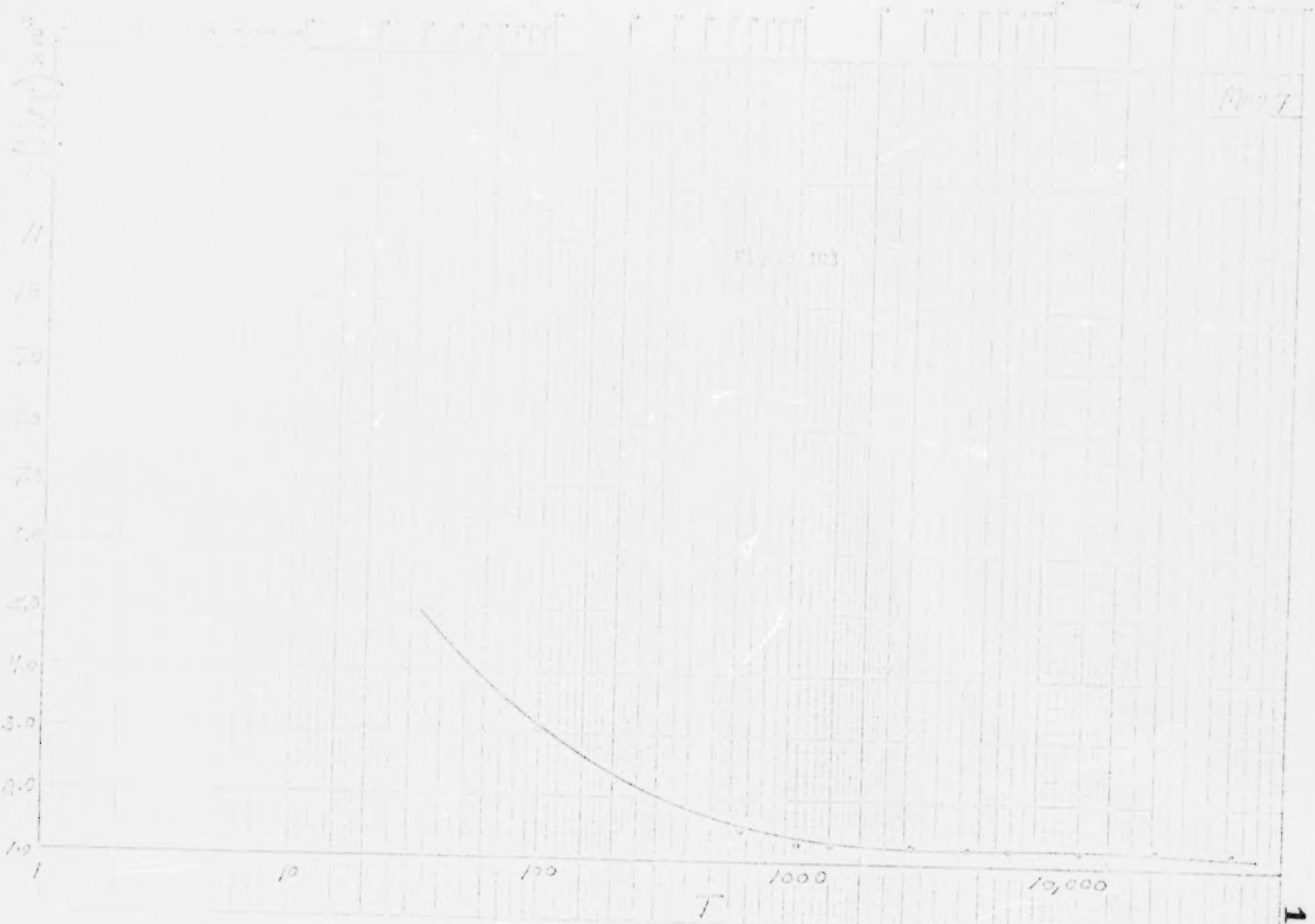
Fig. 7

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THE EFFECT OF CHANGES IN pH ON THE PERFORMANCE OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR

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ABSTRACT

A mathematical model was developed which described the effect of pH on the completely mixed activated sludge system. Experimental data obtained with bench-scale apparatus indicated that the model was of the correct form. The equilibrium constant for the adsorption of H^+ onto activated sludge in an acid environment had an experimentally determined value of 710 $(mg/1)^{-1}$ (pK = 2.85) which was independent of the suspended solids concentration. Difficulty in separating the suspended solids from the reactor effluent prevented accurate measurements of dissolved carbon. Further work remains to be done to determine the effect of pH changes on carbon removal.

INTRODUCTION

During the past twenty years considerable work has been done in the area of waste water treatment. Processing methods have progressed from crude solids separation to sophisticated chemical and biological systems which remove anywhere from sixty to ninety-five percent of the impurities originally present in the waste stream.

The most common biological treatment method is the activated sludge system. In this process, the bacteria present in the waste stream are concentrated into a settleable floc and allowed to react with organic matter dissolved in the waste stream in the presence of dissolved oxygen. The reaction yields a complex mixture of products according to the scheme:

$$\text{bacteria} + \text{carbonaceous waste} \xrightarrow[O_2]{} \text{products}$$

The conventional activated sludge process used long concrete troughs to treat the sewage. This method resembled the plug-flow reactor in which shock loadings are not easily assimilated, causing a feast and famine cycle in which the bacterial floc has either too much or not enough food. The net effect of this process in sewage treatment is that the conversion is not quite as good as might be obtained if the load of organics dissolved in the waste stream were held constant. An improvement in the process can be realized if a completely mixed system is used. Shock loadings are more easily assimilated, and an improved overall removal of pollutants may be had with the completely mixed activated sludge process (CMASP), since the feast and famine cycle is smoothed out. This is not always true for reacting systems, but is a characteristic of the CMASP, giving it a higher overall effectiveness than the conventional system.

Most aspects of this process are well documented in the literature with the exception of pH effects. Although a few studies have been done on the effect of pH on the activated sludge process, they have been qualitative in nature, yielding general observations on the relation of activated sludge efficiency to pH. Rogers and Wilson[14], using nutrient mediums seeded with sewage reached these conclusions on the relation of bacterial growth to pH:

1. Bacterial growth is fastest in the neutral range of pH between 6.5 and 7.5.

2. Bacterial growth is retarded as pH is lowered, stopping completely at pH 3.5.

3. At low pH values (acid medium) yeasts were the prevailing life form; at higher pH's more heterogeneous mixtures of bacteria were present.

Keefer and Meisel[10], who performed a series of experiments with activated sludge on both sides of the neutral range, found that optimum results were obtained close to pH 7. Other investigators have worked with sludges of different origing, reaching similar conclusions. Ruchhoft, et al.[17], studied glucose removal by activated sludge; Levine and Soppeland[12] worked with creamery wastes; Beedham[2] treated wool scouring refuse; Lelonkiewicz[11] looked at sulfite and sulfate waste liquors from a paper mill. All of these observed best waste removal in the near-neutral range, 6.5-7.5.

A marked buffer effect has also been observed on both sides of the neutral range by several workers. Jansky and Ludvik[8] found that although addition of basic tannery wastes inhibited the treatment of municipal wastes, the buffer effect of the activated sludge allowed addition of tannery wastes of ph 11.8 to a biological treatment stream near neutral without increasing the pH of the mixture over 9.0; the ratio of tannery to municipal waste was 2:1. Lelonkiewicz[11] found activated sludge to have a remarkable ability to regulate itself towards a pH of 7. Purice[15], in a study of the fermentation of pharmaceutical plant waste slurries, found that once fermentation had started, the pH was maintained at a constant value of pH 7-8 despite addition of slurries at pH 6.

OBJECTIVES

In order to design an effective pH control system for the CMASP, the dynamics of the system, with respect to time-varient pH changes, must be determined. Up to now, no attempts have been made at finding the dynamic response of the CMASP to pH changes. Previous studies have been performed in batch or plug flow reactors; none have been done with the completely mixed system.

This project was done with two objectives in mind:

1. To determine the dynamic response of the CMASP to step changes in pH.
2. To determine the buffer effect of the CMASP.

DYNAMICS OF STRONG ACID - STRONG BASE SYSTEM

The differential equation describing a completely mixed unsteady-state flow reactor may be written in the form:

$$v \cdot A' - v \cdot A - (-R_A) = V \cdot \frac{dA}{dt} \qquad (1)$$

where

v = constant volumetric flow rate through reactor

V = constant volume of reactor contents

A' = concentration of component A in feed stream

A = concentration of component A in reactor

$(-R_A)$ = rate of disappearance of A

or $(-r_A) = -\frac{dA}{dt} + \frac{(A'-A)}{\theta}$ (2)

$\theta = V/v$ = residence time of reactor

$(-r_A) = (-R_A)/\theta$

In a strong acid - strong base system, it is common to find dissolved CO_2, especially in the basic solution. The dissolved gas exhibits a buffer effect during neutralization because the CO_2 is hydrolyzed to carbonic acid, which further hydrolyzes to form a carbonate-bicarbonate buffer system in the following series of reactions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

The equations which determine the dynamics of a strong acid - strong base neutralization under the influence of the carbonate-bicarbonate buffer are:

$$\underset{A}{H^+} + \underset{B}{OH^-} \rightleftharpoons \underset{R}{H_2O} \qquad K = A \cdot B \tag{3}$$

$$\underset{E}{H_2CO_3} \rightleftharpoons \underset{A}{H^+} + \underset{C}{HCO_3^-} \qquad K_1 = \frac{A \cdot C}{E} \tag{4}$$

$$\underset{C}{HCO_3^-} \rightleftharpoons \underset{A}{H^+} + \underset{D}{CO_3^=} \qquad K_2 = \frac{A \cdot D}{C} \tag{5}$$

If the neutralization is carried out in a completely mixed flow reactor, then a set of ordinary differential equations of the form of equation (2) may be written for each component in the system. The result is the set of simultaneous differential equations:

$$(-r_A) = -\frac{dA}{dt} + \frac{(A'-A)}{\theta} \tag{6}$$

$$(-r_B) = -\frac{dB}{dt} + \frac{(B'-B)}{\theta} \tag{7}$$

$$(-r_C) = -\frac{dC}{dt} + \frac{(C'-C}{\theta} \tag{8}$$

$$(-r_D) = -\frac{dD}{dt} + \frac{(D'-D)}{\theta} \tag{9}$$

$$(-r_E) = -\frac{dE}{dt} + \frac{(E'-E)}{\theta} \tag{10}$$

Inspection of the equations (3), (4), and (5), and the equilibrium constants yields the following additional equations:

$$(-r_A) = (-r_B) + (-r_C) + (-r_D) \tag{11}$$

$$(-r_C) = -(-r_D) - (-r_E) \tag{12}$$

Since $B = \frac{K}{A}$, $\qquad \frac{dB}{dt} = -\frac{K}{A^2}\frac{dA}{dt}$ (13)

$$D = K_2\frac{C}{A} \qquad \frac{dD}{dt} = K_2 \left\{\frac{1}{A}\ \frac{dC}{dt} - \frac{C}{A^2}\ \frac{dA}{dt}\right\} \tag{14}$$

$$E = \frac{A\cdot C}{K_1} \qquad \frac{dE}{dt} = \frac{1}{K_1} \left\{A\frac{dC}{dt} + C\ \frac{dA}{dt}\right\} \tag{15}$$

Substitution of equations (6) - (10) and (13) - (15) into equations (11) and (12) and rearranging yields the final two simultaneous differential equations which describe the system's dynamics:

$$\frac{dA}{dt} = (a - b - z - m + d(z + g + m)/p)/n\cdot k \tag{16}$$

$$\frac{dC}{dt} = (z + g + m + r(a - b - z - m)/n)/p\cdot k \tag{17}$$

where

$a = (A' - A)/\theta$ $\qquad$ $b = K(1/A' - 1/A)/\theta$

$g = (A'\cdot C' - A\cdot C)/\theta\cdot K_1$ $\qquad$ $d = (1 - K_2/A)$

$n = 1 - K/A^2 - K_2\cdot C/A^2$ $\qquad$ $g = (C' - C)/\theta$

$r = K_2\cdot C/A^2 - C/K_1$ $\qquad$ $p = 1 + A/K_1 + K_2/A$

$k = 1 - d\cdot r/n\cdot p$

These equations are conveniently solved for pH as a function of time with the aid of a digital computer. Initial and boundary conditions which must be known to solve the equations are:

A' = concentration of A in the feed stream

C' = concentration of C in the feed stream

A_o = concentration of A in the reactor at time = 0

C_o = concentration of C in the reactor at time = 0

θ = residence time

K, K_1, K_2 = equilibrium constants

Rather than specify the concentration of C in the feed stream and reactor, it would be easier to specify the total concentration of inorganic carbon, which can be measured with an infrared analyzer as CO_2. The CO_2 present in solution is the sum of the three inorganic species, H_2CO_3, HCO_3^-, $CO_3^=$.

$$\underset{TIC}{CO_2} = \underset{E}{H_2CO_3} + \underset{C}{HCO_3^-} + \underset{D}{CO_3^=} \qquad (18)$$

Expressions for E and D in terms of component C can be found by rearranging the equilibrium expressions for K_1 and K_2. Substitution of these terms into equation (18) and rearrangement yields the equation for C (HCO_3^-) in terms of total inorganic carbon and hydrogen ion concentrations, both of which can be measured experimentally. Therefore, $C = TIC/(1 + A/K_1 + K_2/A)$ (19)

If the expression for C is divided by TIC, the resulting equation gives the fraction of the total inorganic carbon which is in the form of bicarbonate ion as a function of the equilibrium constants K_1 and K_2 and the hydrogen ion concentration (A):

$$f_C = 1/(1 + A/K_1 + K_2/A) \qquad (20)$$

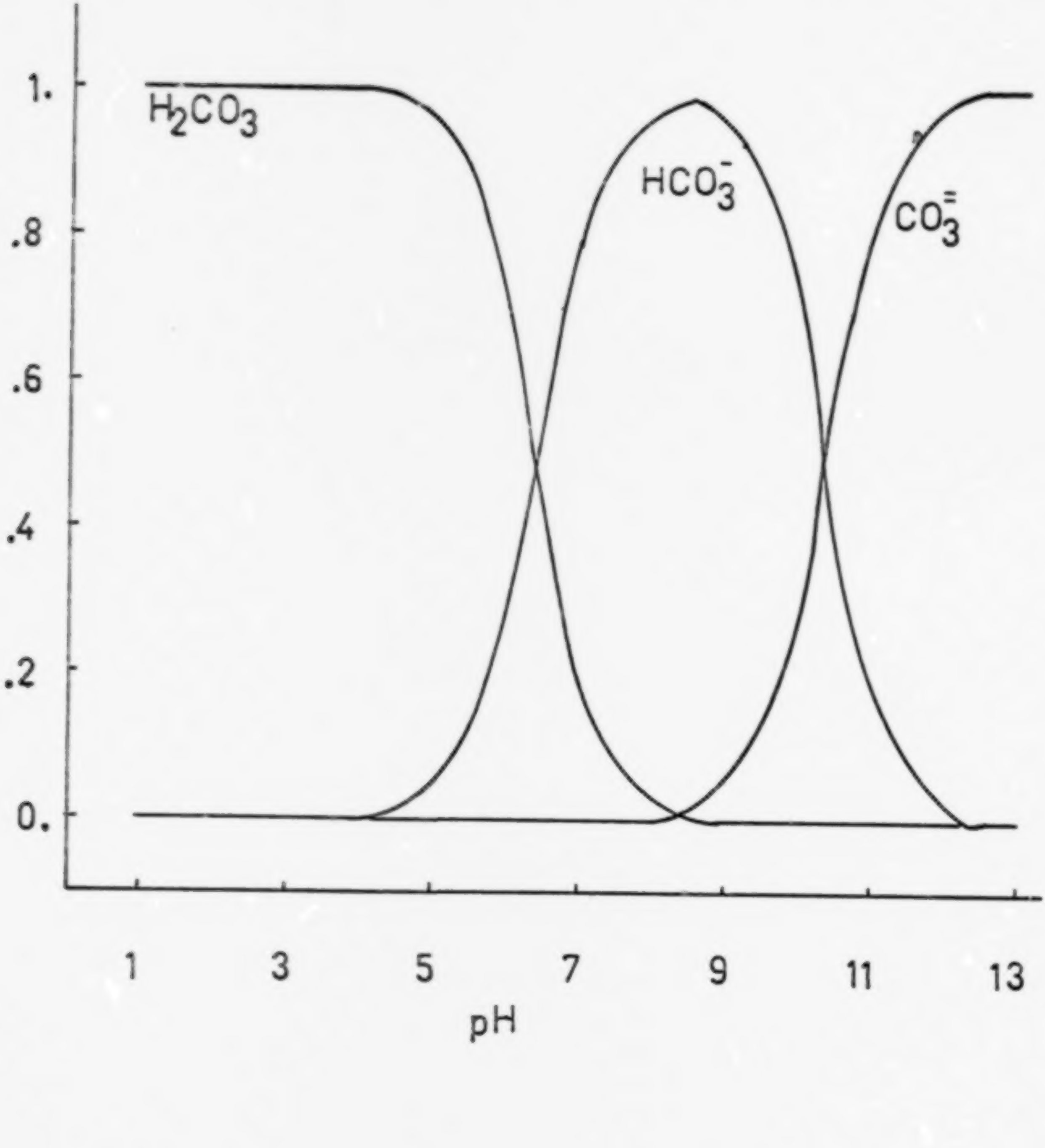
Expressions for the fractions of carbonate ion and carbonic acid may be derived in a similar manner:

$$f_D = 1/(1 + A/K_1 + A^2/K_1 \cdot K_2) \qquad (21)$$

$$f_E = 1/(1 + K_1/A + K_1 \cdot K_2/A^2) \qquad (22)$$

Fig. 1 shows plots of the fractions of H_2CO_3, HCO_3^-, and $CO_3^=$ versus pH.

Figure 1 - Fractions of H_2CO_3, HCO_3^-, and $CO_3^=$ as a Function of pH



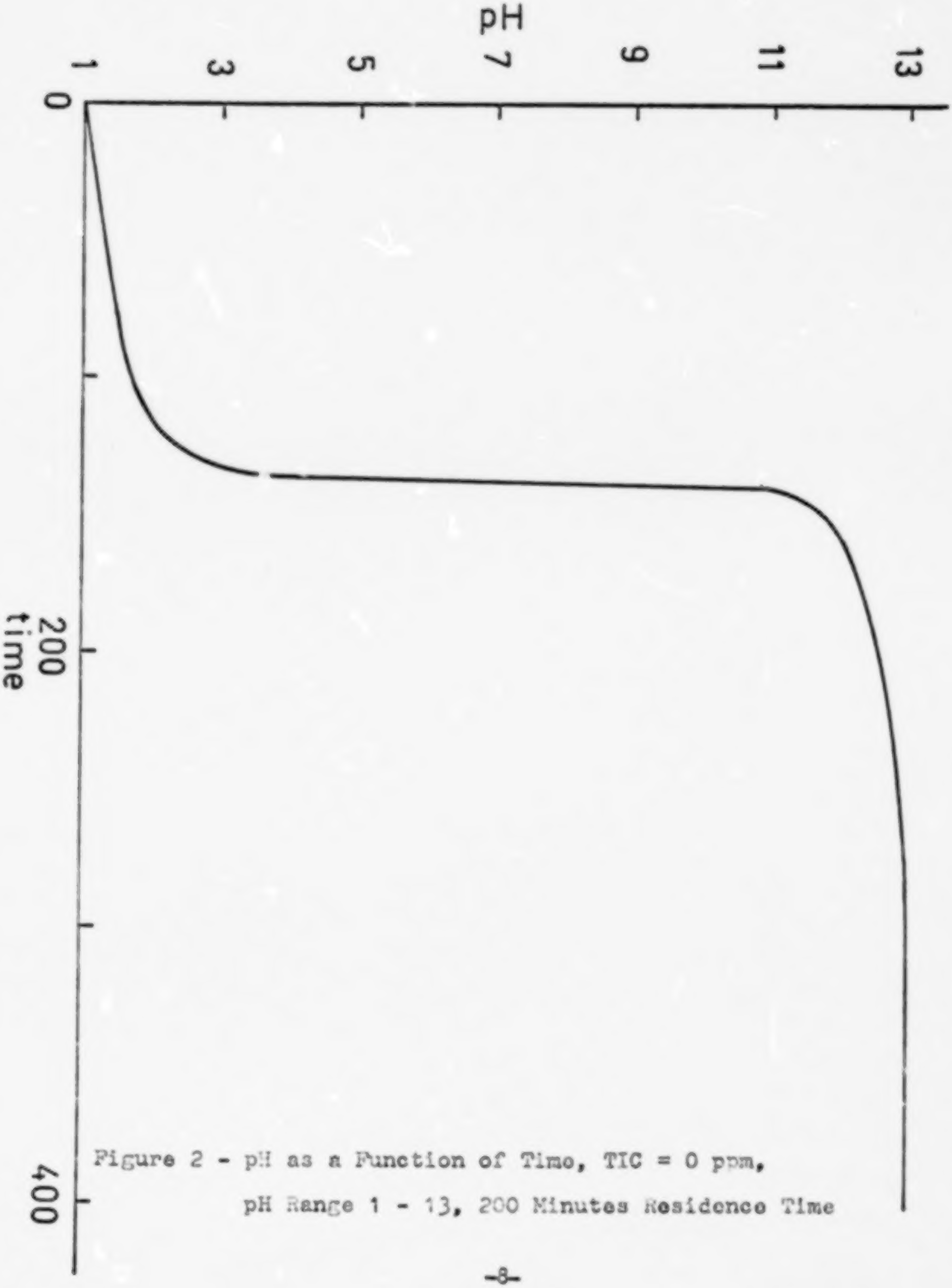


Figure 2 - pH as a Function of Time, TIC = 0 ppm,
pH Range 1 - 13, 200 Minutes Residence Time

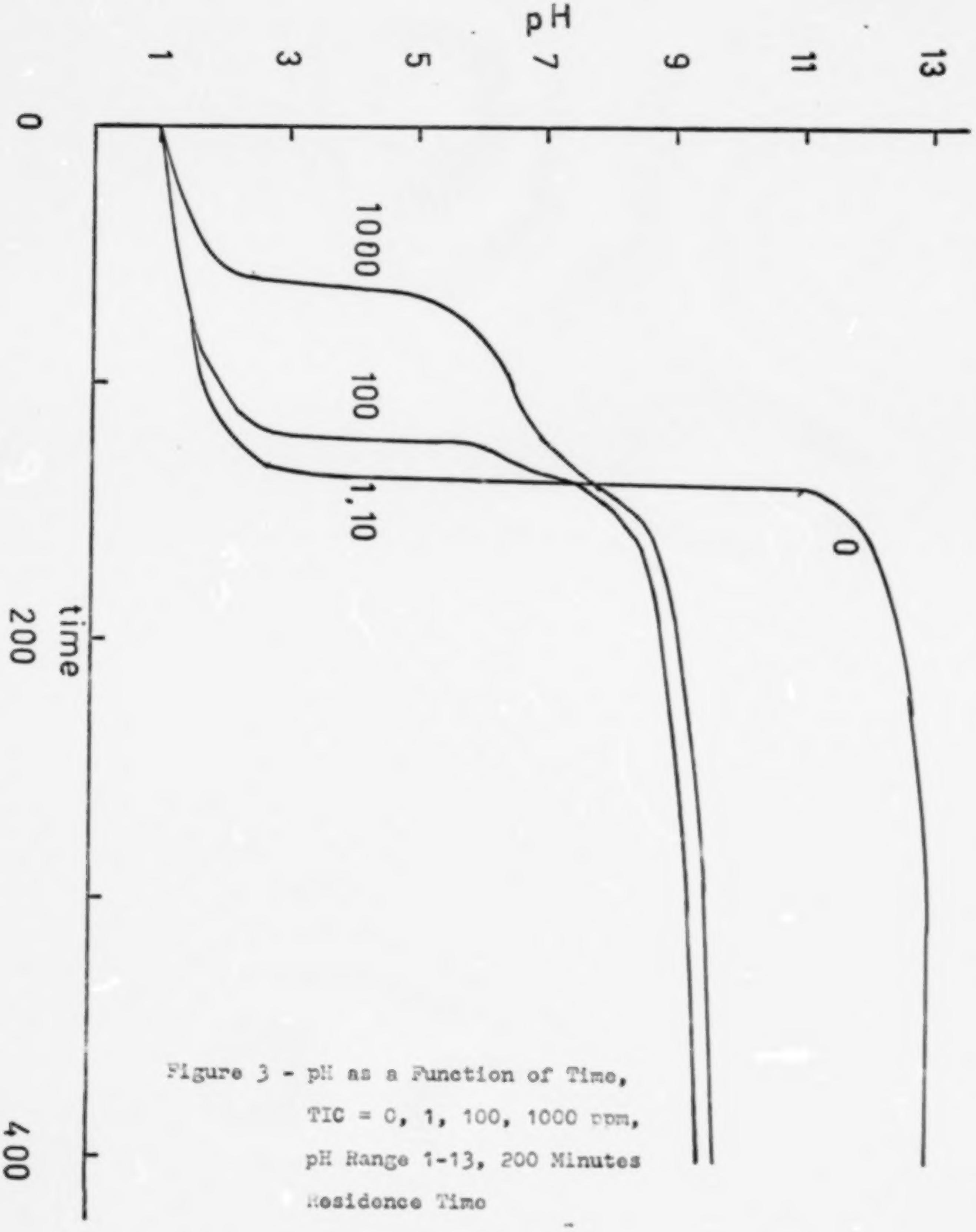


Figure 3 - pH as a Function of Time, TIC = 0, 1, 100, 1000 ppm, pH Range 1-13, 200 Minutes Residence Time

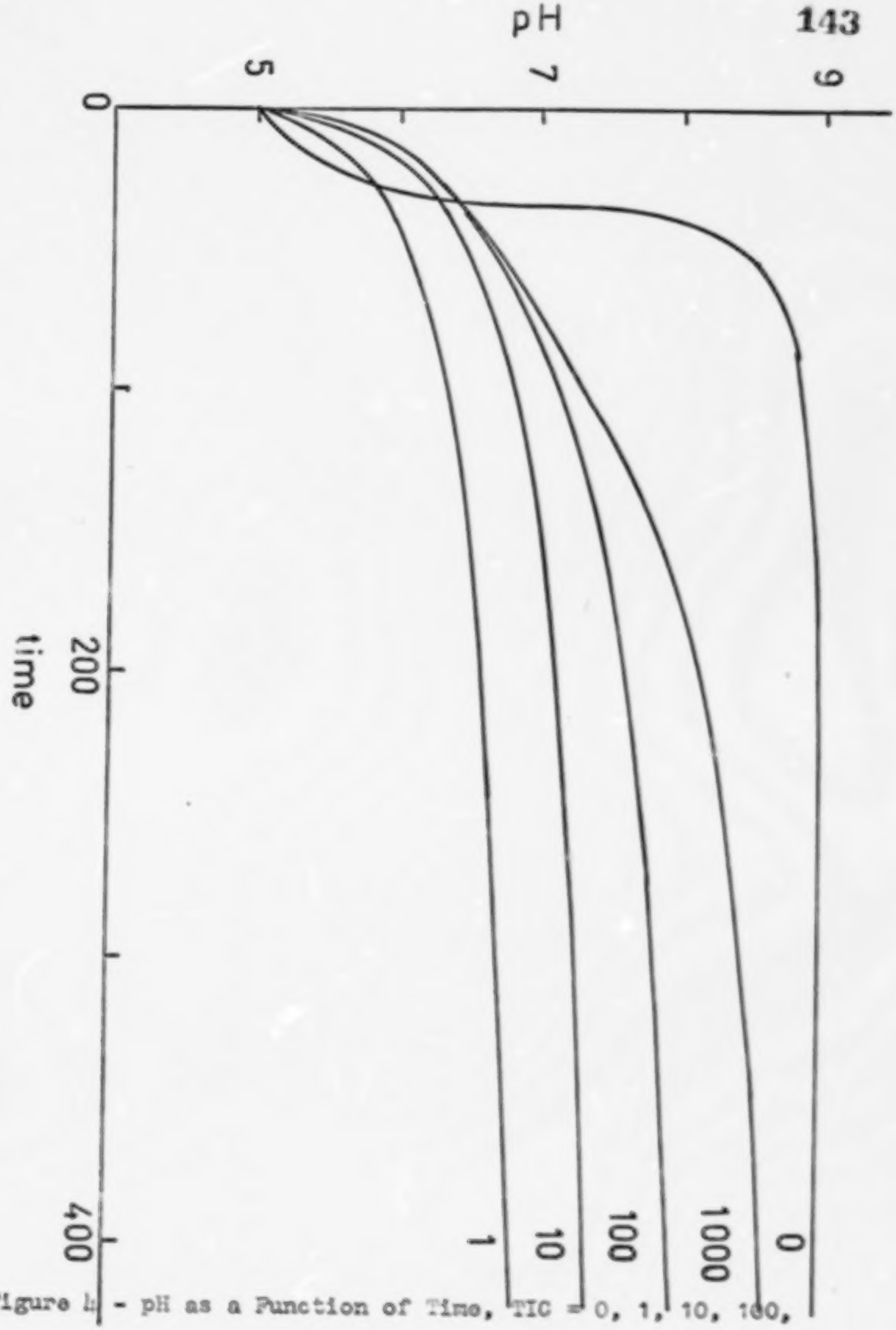


Figure 4 - pH as a Function of Time, TIC = 0, 1, 10, 100, 1000 ppm, pH Range 5-9, 50 Minutes Residence Time

The effect of the buffer can best be described by comparing it to the case of the unbuffered system. For the unbuffered case, the equations are obtained by setting C' and C_o equal to zero. For this case, a plot of pH versus time for a strong acid (HCl) - a strong base (KOH) neutralization with a constant flow rate of 0.1-N base (pH=13) being added to a reactor initially containing 0.1-N acid (pH=1) is represented by the curve of Fig. 2. As the TIC concentration is increased from zero, the shape of the neutralization curve gradually changes to reflect the increasing buffer capacity, and two new equivalence points for H_2CO_3 and HCO_3^- are introduced. Fig. 3 shows the pH versus time curves for TIC concentrations of 1, 100, and 1000 ppm of inorganic carbon in the buffered system. With 1 ppm TIC present, the system exhibits no difference from the unbuffered case until pH 7.5, where the buffered curve flattens out, while the 0 ppm TIC curve continues rising sharply. At 100 ppm TIC a more rapid initial rise in pH takes place at first, the equivalence point for H_2CO_3 appears at pH 6.3 and the curve becomes identical with the 1 ppm curve at pH 7.5. At 1000 ppm TIC an even more rapid initial rise in pH occurs, while the equivalence point for H_2CO_3 becomes even more evident at pH 6.3. The rapid initial rise in pH for the buffered system is due to the fact that at the feed pH (13) the inorganic carbon is all in the $CO_3^=$ form, while that in the reactor (pH=1) is all in the acid form. Complete neutralization of the $CO_3^=$ ion to H_2CO_3 requires two hydrogen ions in addition to the one required to neutralize the OH^- being added. As the TIC is increased this effect becomes more pronounced, as evidenced by the curves in Fig. 3.

The pH range of 5-9 is of special interest since activated sludge systems normally operate here. The effect of TIC concentration is seen in Fig. 4 which shows the neutralization curves for concentrations of 0, 1, 10, 100, and 1000 ppm of TIC. Each one is a distinct curve, and contrary to the case of the pH 1-13 region, the buffered system requires more time to reach pH 7 then the unbuffered system.

DYNAMICS OF ACTIVATED SLUDGE SYSTEM

For the completely mixed activated sludge system the same basic equations apply as for the acid-base system; that is, equations of the form (2) may be written for each component of the system, and the same kinetic equations may be written for the hydrolysis of dissolved CO_2. In addition, a material balance may be written for the sludge:

$$(-r_S) = -\frac{dS}{dt} + \frac{(S'-S)}{\theta}$$

where:

S' = concentration of sludge in the feed

S = concentration of sludge in the reactor

Since for this system the concentration of sludge in the system is almost constant for all practical purposes, the solution of the sludge balance is:

$$(-r_S) = (S'-S) = (dS/dt) = 0$$

In addition to the buffer effect of the CO_2, it may be possible for hydrogen ion to be adsorbed on the bacterial floc, or sludge, according to the reaction:

$$H^+ + S \rightleftharpoons H{\cdot}S^+ \qquad K_3 = \frac{(H{\cdot}S^+)}{(H^+)(S)}$$

This reaction adds an extra equation to the scheme presented for the acid-base dynamics. The equations now become:

$$\underset{A}{H^+} + \underset{B}{OH^-} \rightleftharpoons \underset{R}{H_2O} \qquad K = A{\cdot}B \tag{3}$$

$$\underset{E}{H_2CO_3} \rightleftharpoons \underset{A}{H^+} + \underset{C}{HCO_3^-} \qquad K_1 = \frac{A{\cdot}C}{E} \tag{4}$$

$$\underset{C}{HCO_3} \rightleftharpoons \underset{A}{H^+} + \underset{D}{CO_2^=} \qquad K_2 = \frac{A{\cdot}D}{C} \tag{5}$$

$$\underset{A}{H^+} + \underset{S}{S} \rightleftharpoons \underset{W}{H{\cdot}S^+} \qquad K_3 = \frac{W}{(A)(S)} \tag{20}$$

Inspection of equations (3) - (5) and (20) and the equilibrium expressions yield the equations:

$$(-r_A) = (-r_B) + (-r_C) + (-r_D) - (-r_W) \tag{21}$$

$$(-r_C) = -(-r_D) - (-r_E) \tag{22}$$

$$W = \frac{K_3}{(A)(S)} \qquad \frac{dW}{dt} = \frac{-K_3}{(S)(A)^2} \quad \frac{dA}{dt} \tag{23}$$

Making a material balance for component W:

$$(-r_W) = -\frac{dW}{dt} = \frac{(W'-W)}{\theta} \tag{24}$$

Substitution and rearrangement similar to that in the previous section yield the two simultaneous differential equations which describe the system dynamics in terms of A and C:

$$\frac{dA}{dt} = \frac{(a - b - z - m + h + d(z + g + m)/p)}{n \cdot k} \tag{25}$$

$$\frac{dC}{dt} = \frac{(z + g + m + r(a - b - z - m + h)/n)}{p \cdot k} \tag{26}$$

where:

$$h = \frac{K_3}{S \cdot \theta} \;(1/A' - 1/A) = \frac{K_3 \cdot b}{S}$$

$$n = 1 + K/A^2 + K_2 \cdot C/A^2 + K_3/S \cdot A^2$$

and the remaining variables remain the same as those described for the acid-base system. However, this leaves a gap in the description of the dynamics of the system; since K_3 is unknown the response of the activated sludge process to pH changes cannot be predicted.

Although K_3 cannot be predicted from purely theoretical considerations, it may be obtained from experimental data. Consider two sludge samples of identical volume V, identical in every respect except total solids concentrations. If both samples are titrated with an acid solution of known strength, a plot of pH of the solution versus the milliequivalents of H^+ added may be obtained for each sample. The first sample, with total solids concentration $TS_1 = 0$, may be used as a reference, or blank sample. The second sample, with a known solids concentration TS_2, will have the reaction,

$$H^+ + S \rightleftharpoons H \cdot S^+$$

occurring in addition to those which take place in the first case. Typical titration curves are shown in Figure 5. To reach the point designated by pH_a in Figure 5, n_1 equivalents of H^+ must be added to sample 1, while n_2 equivalents must be added to sample 2. Since the samples are identical except for the different total solids concentrations, the difference $(n_2 - n_1)$ is a measure of the amount of protonated sludge $(H \cdot S^+)$ present in the second sample. If the quantity Δ is defined as $(n_2 - n_1)/V$, then the normalized quantity Δ/TS_2, with units of meq. of H^+ added per mg. of solids, may also be defined. When Δ/TS_2 is plotted versus pH, as in Figure 6, it is seen to be a unimodal function, which is zero at the start of the titration, rises to a maximum where curve 2 and the reference curve are furthest apart, and then drops back to zero as the two curves meet again at some low pH. As the total solids concentration in sample 2 is increased, the value of Δ at pH_a should also increase, but the quantity Δ/TS_2, being a normalized function, will remain constant for any total solids concentration.

An approximation of K_3 may be obtained from the normalized curve if the assumption is made that at the maximum value of Δ/TS all of the available sludge has been converted to the protonated form, $H \cdot S^+$. Then the equilibrium constant may be obtained by finding the half-neutralization point on the curve of Fig. 6. Since $(S) = (H \cdot S^+)$ at the half-neutralization point, K_3 may be calculated from the expression:

$$K_3 = \frac{1}{(H^+)}$$

or

$$-\log K_3 = pK_3 = -\log (H^+) = pH$$

The effect of the pH changes on the rate of consumption of organic carbon in the waste stream may also be found. The material balance on total organic carbon (TOC) may be written in the form of equation (2),

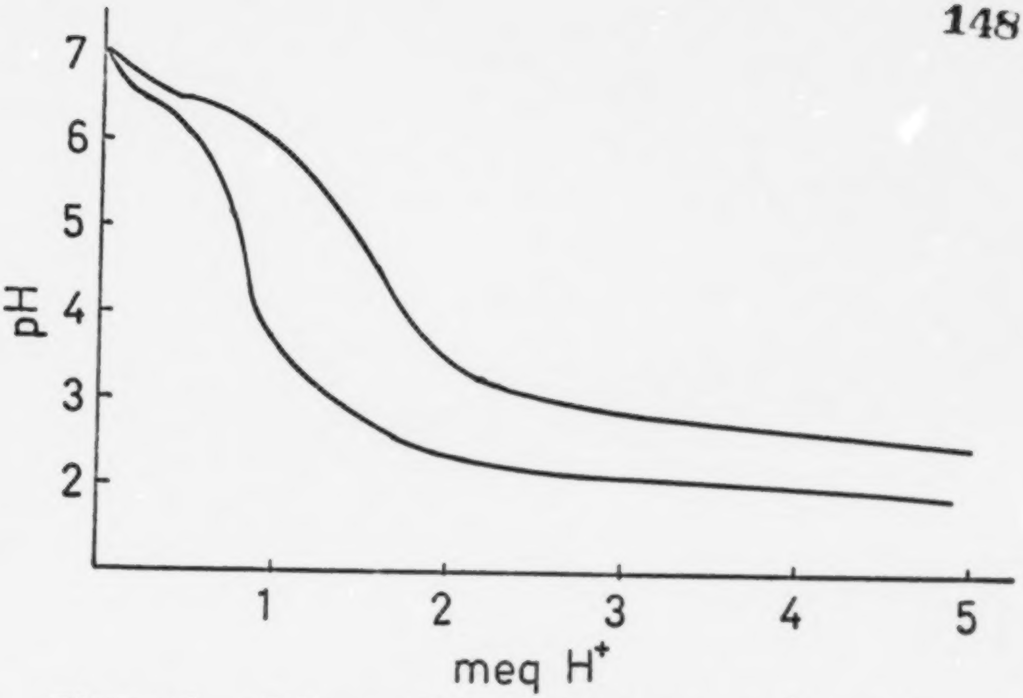
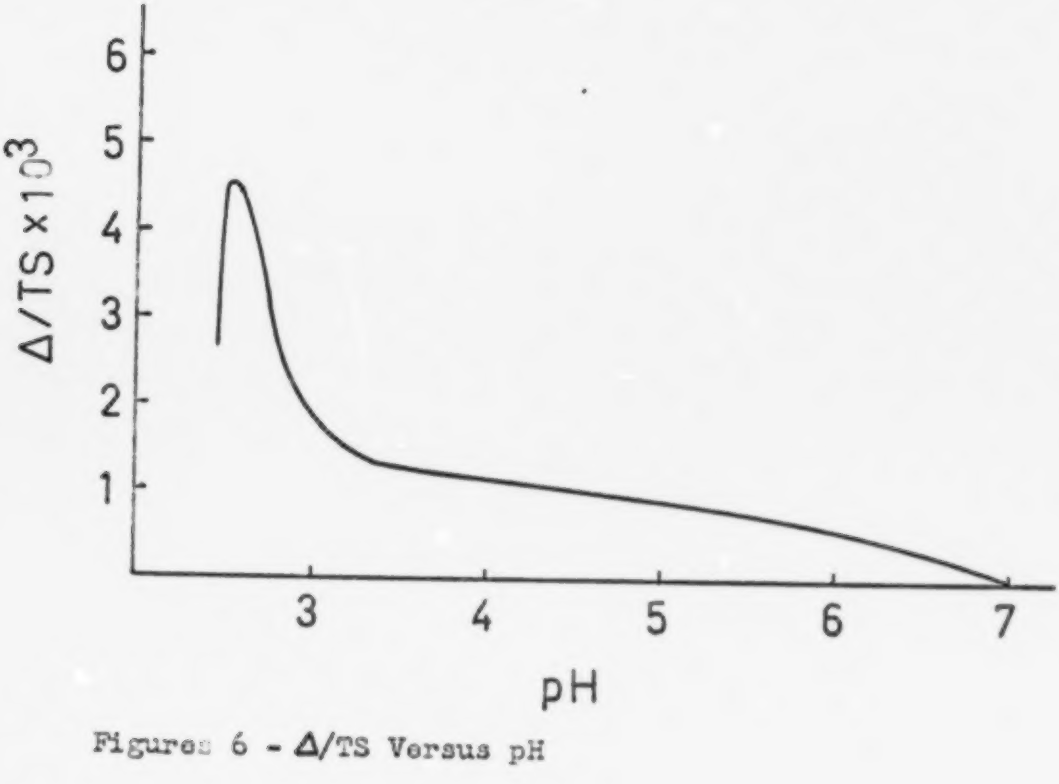


Figure 5 - pH Versus Milliequivalents of H$^+$ Added



Figures 6 - Δ/TS Versus pH

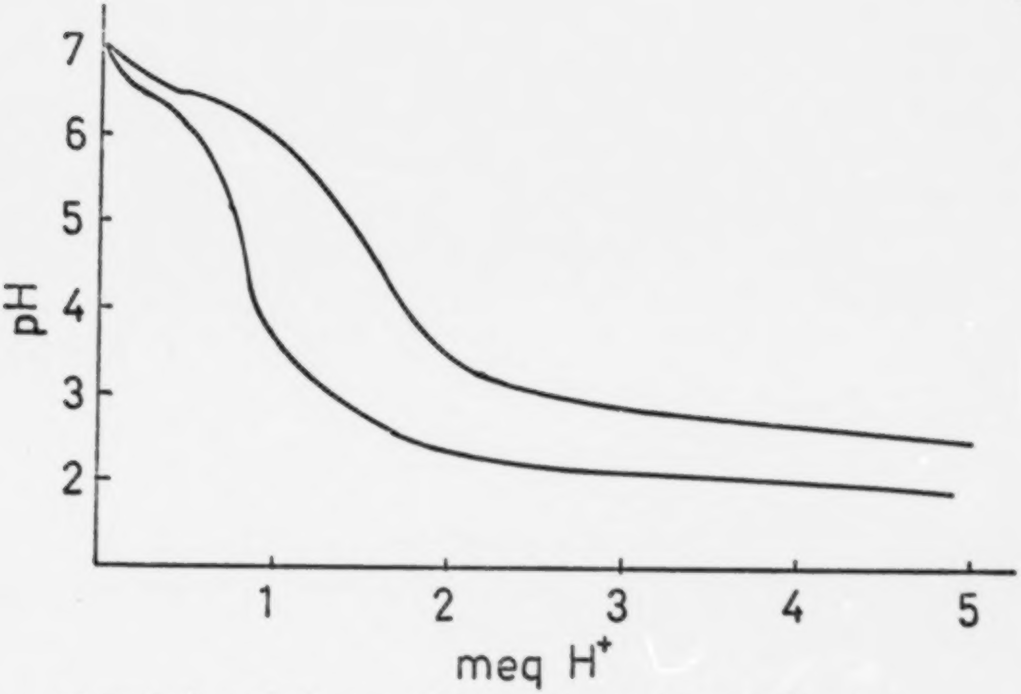
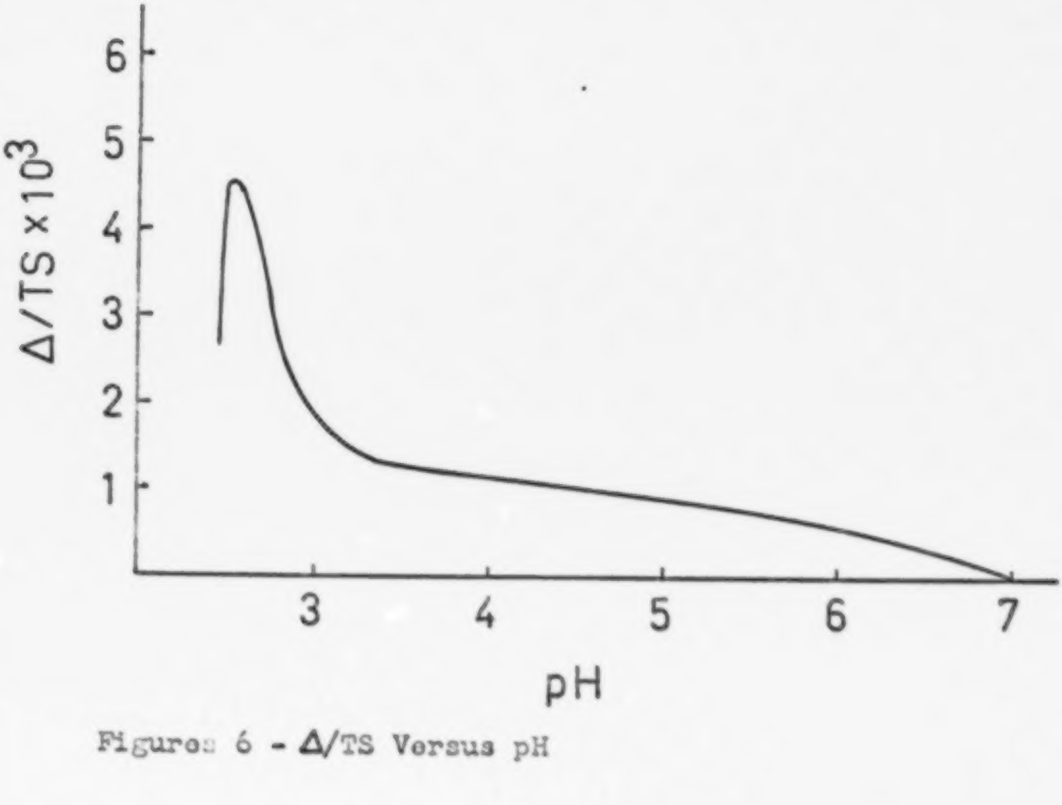


Figure 5 - pH Versus Milliequivalents of H^+ Added



Figures 6 - Δ/TS Versus pH

$$(r_{Ca}) = -\frac{dCa}{dt} - \frac{(Ca'-Ca)}{\theta} \qquad (27)$$

The kinetics of the biological reaction where dissolved carbon is converted to products may be represented by the expression:

$$(-r_{Ca}) = k(Ca)(S) \qquad (28)$$

where:

Ca' = concentration of dissolved carbon in the feed

Ca = concentration of dissolved carbon in the reactor

k = reaction rate constant for the carbon to products reaction.

To obtain the constant, k, as a function of pH, equation (27) is calculated at steady state conditions for various pH levels. Equation (28) may then be used to calculate the reaction rate constant, k, for each data point, and these values of k may be fitted by an appropriate method as a function of pH.

The method used to determine K_3 for activated sludge may be justified by showing that it applies to other systems as well, in particular the carbonate - bicarbonate buffer system. Since the equilibrium constants for this system are already known, the course of a titration may be calculated by a computer program rather than obtained experimentally. Results were obtained for solutions containing 0, 1, 5, 10, and 50 ppm of inorganic carbon as carbonate. The calculations were started at pH=7.0, and 0.1^N acid was added at a constant rate of 1.0 cc/min to a 1-liter solution. Results from the program were plotted as curves of pH versus milliequivalents of H^+ added as shown in Fig. 6A.

The number of milliequivalents of H^+ required to bring each sample to a particular pH may be obtained from the titration curves. In Fig. 6A, for example, the values H_0, H_1, H_5, H_{10}, and H_{50} are the number of meq of H^+ required to bring 1 liter samples with TIC concentrations of 0, 1, 5, 10, and 50 ppm respectively, to pH_a. The amount of H^+ consumed by the buffer alone in a particular sample may be calculated by subtracting the total amount of H^+ required for

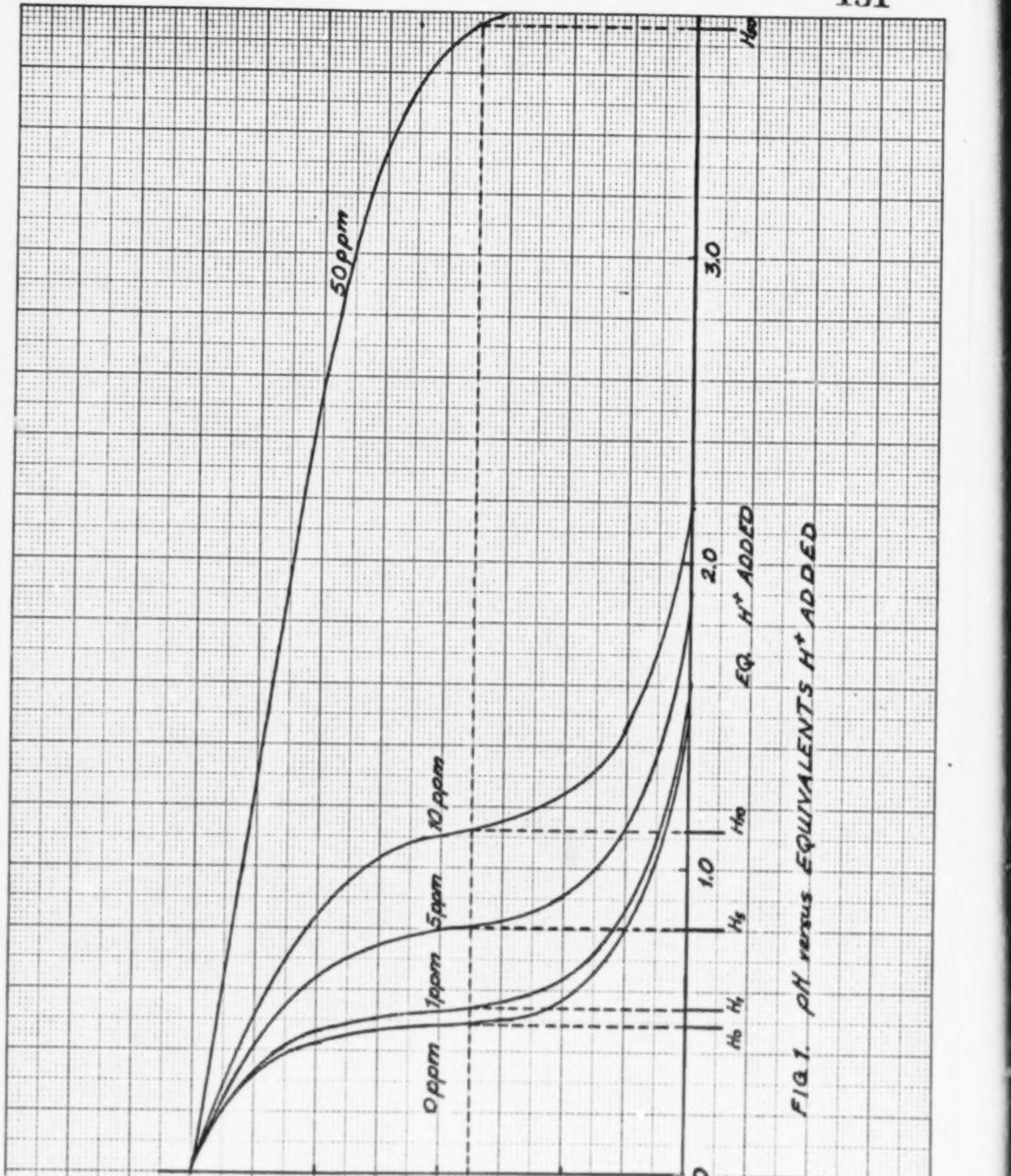


FIG. 1. pH versus EQUIVALENTS H^+ ADDED

K&E 10 X 10 TO 1/2 INCH 46 1470
KEUFFEL & ESSER CO.

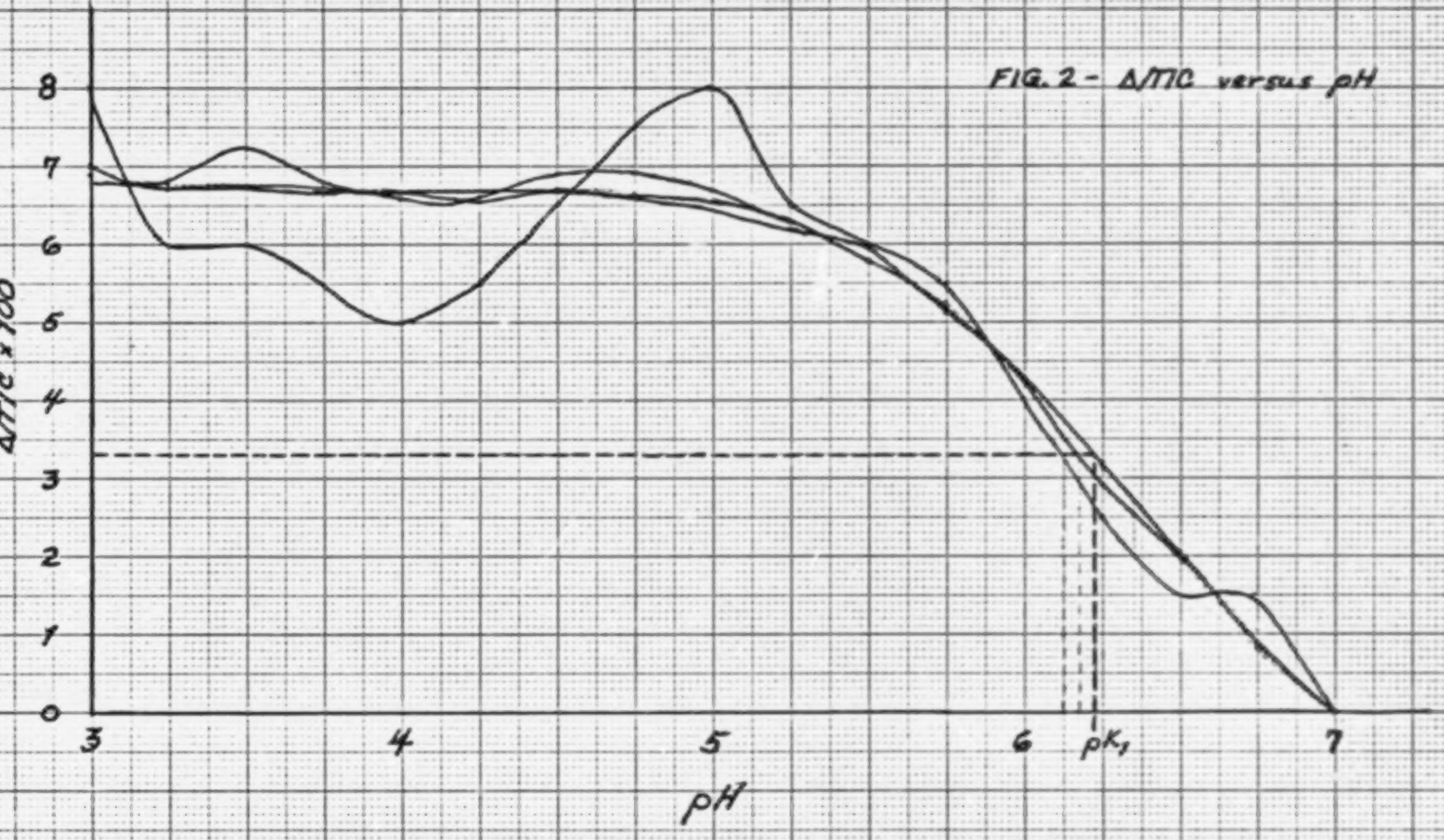


FIG. 2 - ΔT/TC versus pH

K&E 10 X 10 TO 1/2 INCH 46 1470
7 1/2 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

the unbuffered sample (H_0) from the total amount required by the buffered sample (H_n). This difference ($H_n - H_0$) is designated by the symbol Δ . Dividing the quantity by the total inorganic carbon concentration (TIC) results in the normalized quantity Δ/TIC which is independent of TIC. Table 1 gives values of H_n, Δ , and Δ/TIC in the range pH 7.0 - pH 3.0. The equilibrium constant can be derived from a plot of Δ/TIC in the following manner. If it is assumed that the maximum value of Δ/TIC occurs at the end point of the titration, then the half-neutralization point will occur at a value of Δ/TIC equal to half the maximum value. The first equilibrium constant for the carbonate-bicarbonate buffer system may be defined by:

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)}$$

At the half-neutralization point, $(HCO_3^-) = (H_2CO_3)$, therefore, $K_1 = (H^+)$. Taking the logarithm of both sides of the last equality would give after rearrangement, $pK_1 = pH$. The value of pK_1 for the carbonate-bicarbonate buffer system is 6.36, while the value obtained by this method is 6.21. The close agreement between the accepted and estimated values of pK_1 indicates the validity of the method, which can now be applied to other systems to determine unknown constants.

TABLE 1

pH	H_0	H1	H5	H10	H50	Δ1	Δ5	Δ10	Δ50
7.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
6.75	0.205	0.220	0.250	0.290	0.640	0.015	0.045	0.085	0.435
6.50	0.320	0.335	0.420	0.525	1.330	0.015	0.100	0.205	1.010
6.25	0.390	0.415	0.535	0.710	1.945	0.025	0.145	0.320	1.555
6.00	0.420	0.460	0.635	0.845	2.540	0.040	0.215	0.425	2.120
5.75	0.440	0.495	0.700	0.965	3.020	0.055	0.260	0.525	2.580
5.50	0.450	0.510	0.740	1.030	3.335	0.060	0.290	0.580	2.985
5.25	0.455	0.520	0.770	1.080	3.555	0.065	0.315	0.625	3.100
5.00	0.460	0.540	0.795	1.115	3.680	0.080	0.335	0.655	3.220
4.75	0.475	0.550	0.820	1.140	3.760	0.075	0.345	0.665	3.285
4.50	0.500	0.565	0.845	1.170	3.825	0.065	0.345	0.670	3.325
4.25	0.540	0.595	0.870	1.195	3.880	0.055	0.330	0.655	3.340
4.00	0.580	0.630	0.910	1.245	3.925	0.050	0.330	0.665	3.345
3.75	0.655	0.710	0.995	1.320	4.025	0.055	0.340	0.665	3.370
3.50	0.790	0.850	1.130	1.465	4.170	0.060	0.360	0.675	3.380
3.25	1.040	1.100	1.380	1.710	4.430	0.060	0.340	0.670	3.390
3.00	1.480	1.560	1.830	2.170	4.875	0.080	0.350	0.690	3.395

pH	Δ/TIC1	Δ/TIC5	Δ/TIC10	Δ/TIC50
7.00	0.000	0.000	0.000	0.000
6.75	0.015	0.009	0.008	0.009
6.50	0.015	0.020	0.020	0.020
6.25	0.025	0.029	0.032	0.031
6.00	0.040	0.043	0.042	0.042
5.75	0.055	0.052	0.052	0.052
5.50	0.060	0.058	0.058	0.060
5.25	0.065	0.063	0.062	0.062
5.00	0.080	0.067	0.065	0.065
4.75	0.075	0.069	0.066	0.066
4.50	0.065	0.069	0.067	0.067
4.25	0.055	0.066	0.065	0.067
4.00	0.050	0.066	0.067	0.067
3.75	0.055	0.068	0.067	0.067
3.50	0.060	0.072	0.067	0.068
3.25	0.060	0.068	0.067	0.068
3.00	0.080	0.070	0.069	0.068

EXPERIMENTAL METHOD - ACID-BASE SYSTEM

The reactor was filled with tap water and the pH was adjusted to a value close to 5. A supply bottle of tap water was adjusted to a pH of 10. With the mixer in the reactor turned on, the pH in the reactor was recorded until it had reached a steady value. At this time the feed pump was turned on to feed base into the reactor at a constant rate. The pH of the input and the reactor were continuously recorded. The effluent of the reactor was fed through the Union Carbide CO_2 analyzer, which took a sample and analyzed it for total carbon once every four minutes.

EXPERIMENTAL METHOD - ACTIVATED SLUDGE SYSTEM

Prior to an experimental run, several gallons of fresh primary effluent were collected from The University of Connecticut sewage plant. The sewage was filtered and placed in a refrigerator to prevent any deterioration. At the same time, a supply of fresh sludge was collected from a pilot plant at the treatment facility which was operated to generate sludge for these experiments.

At the start of an experiment, a portion of the filtered sewage was treated with either acid or base to bring it to the appropriate pH of the pH variable stream. The reactor was filled with the combined sludge-sewage feed and run until pH, total carbon, and sludge concentration had reached a steady-state value in both the input stream and the reactor. Once steady state was achieved, the input pH was stopped while the sludge and total carbon were held constant in the mixed feed stream. Thus, the effect of the pH change was not masked by an interfering effects due to changes in sludge or carbon concentration. Step changes were made using the Phoenix Varipump by attaching a step-change pattern to the revolving drum on the pump.

The mixed feed stream was fed at such a rate that the residence time in the reactor was about two hours. Both input and reactor pH were recorded continuousl during the experiment. Samples of effluent were analyzed for total carbon every four minutes, and samples of the mixed feed stream were filtered and analyzed once every hour during a run to make sure that no significant deterioration occurred while the experiment was in progress.

Both the sewage and the pH variable supply of sewage were kept in polyehtylene bottles in a refrigerator to prevent any deterioration during the course of an experimental run. The sludge was kept in a polyethylene bottle placed in an ice bath for the same reason. All three feed reservoirs were kept completely mixed at all times to avoid any gradient in concentration which might have occurred dur to settling of the sludge or any colloidal particles which might remain in the sewage after filtering.

EXPERIMENTAL APPARATUS - ACID-BASE SYSTEM

The reactor was constructed from a three-liter pyrex beaker divided into two sections by a vertical glass plate, which was sealed to the sides and bottom of the beaker with a chemically inert epoxy resin. The feed to the reactor consisted of one stream of water, the pH of which was held constant over an entire run. This stream was fed to the reactor through ¼" O.D. polyehtylene tubing by a Harvard Apparatus model 955 continuous infusion-withdrawal pump.

The pH of both the input stream and the reactor contents were measured with Beckman process pH electrodes; the pH of the input stream was read from a Fisher Accumet pH meter and recorded on an L & N model H strip chart recorder, while the pH of the reactor contents was read with a Beckman Instruments model 900 pH analyzer and recorded on an Esterline Angus model E1101E strip chart recorder. The reactor effluent was fed through a Union Carbide model 1201 Total Carbon Analyzer connected to a Beckman IR315 infrared analyzer which measured the amount of carbon in the system as CO_2.

EXPERIMENTAL APPARATUS - ACTIVATED SLUDGE SYSTEM

The same reactor was used for both the acid-base and the activated sludge studies.

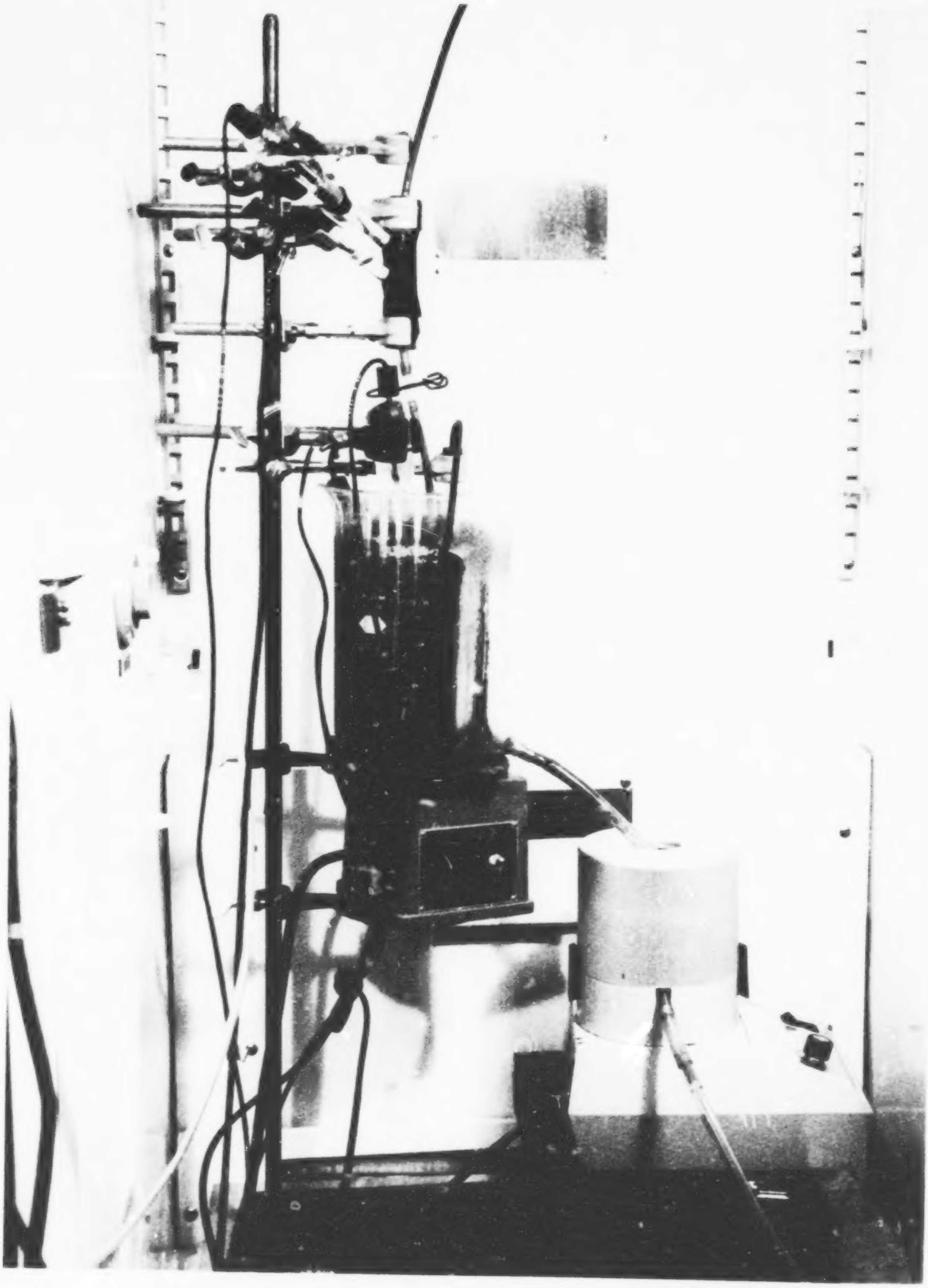
The feed to the reactor consisted of three separate streams which were combined before being fed into the system; a sewage stream, a sludge stream, and a variable pH sewage stream. The sewage stream was filtered primary effluent from The University of Connecticut treatment plant. It was fed to the system through ¼" O.D. polyethylene tubing by a Harvard Apparatus model 955 continuous infusion-withdrawal pump. The sludge stream, consisting of settled sludge from The University of Connecticut treatment plant, was fed to the system through ¼" O.D. Tygon tubing by a Sigmamotor model T-8 pump driven by a Graham model 20AMT37 variable speed transmission. The variable pH stream was made up of primary sewage to which either acid or base had been added to bring the stream to the proper pH. This stream was fed to the system by a Phoenix Precision Instrument Varipump, which automatically varied the pH of the stream according to a curve traced on a revolving drum.

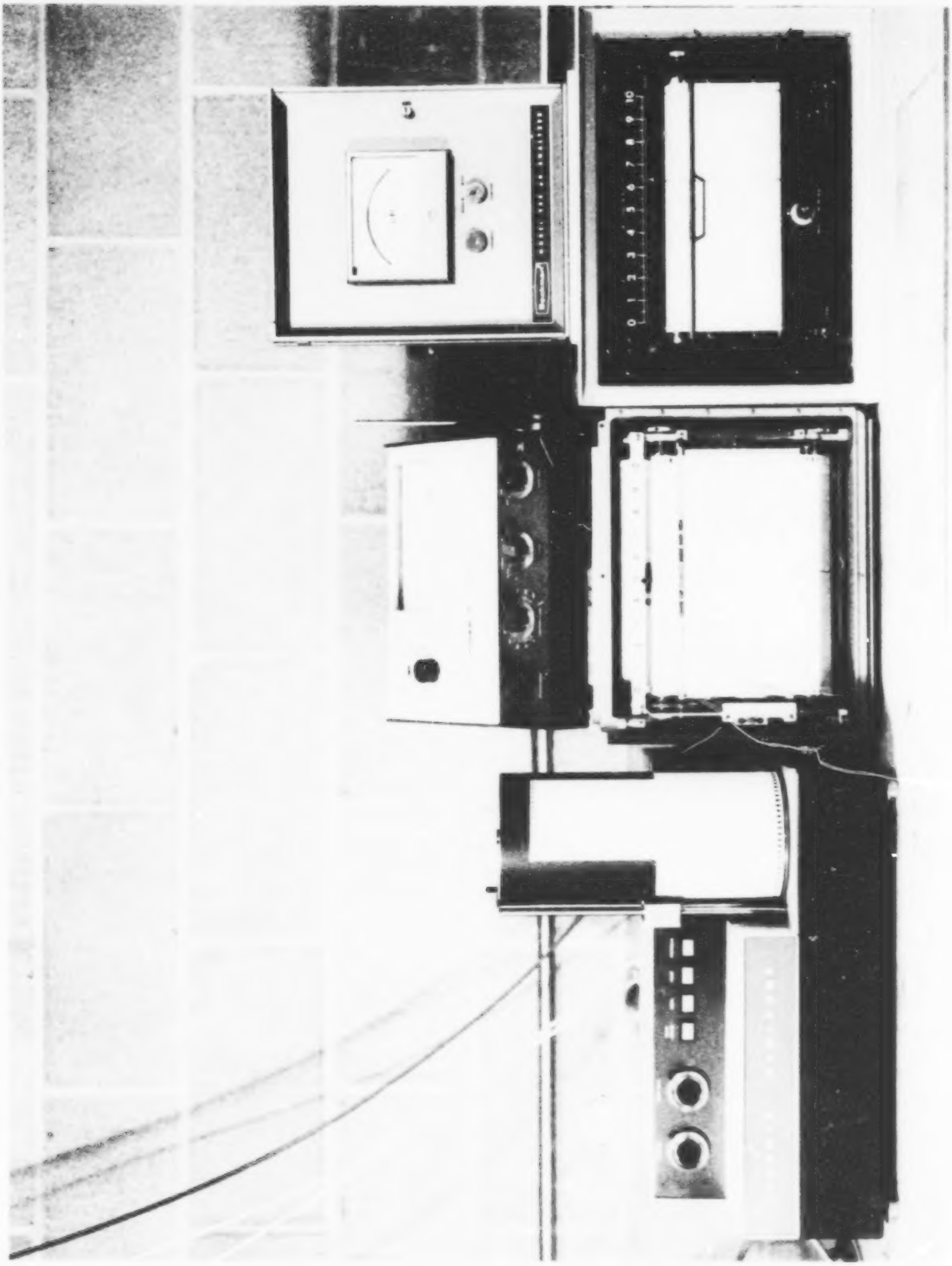
The streams from each of the three pumps were mixed before being fed to the reactor system, and the pH of this combined stream was designated as the input pH. The pH of both the input stream and the reactor were measured with Beckman process pH electrodes; the pH of the input stream was read from a Fisher Accumet pH meter and recorded on an L & N model W strip chart recorder, while the pH of the reactor contents was read with a Beckman Instruments model 900 pH analyzer and recorded on an Esterline Angus model E1101E strip chart recorder. The effluent from the system was fed to a CRC Filtermatic 1001/71 continuous centrifuge, in which the solid sludge was separated. The liquid stream was then fed through a Union Carbide 1201 Total Carbon analyzer. At four-minute intervals, the analyzer automatically injected a 40-μ l sample of the liquid into a Vycor tube through which a stream of Nitrogen carrier gas was flowing.

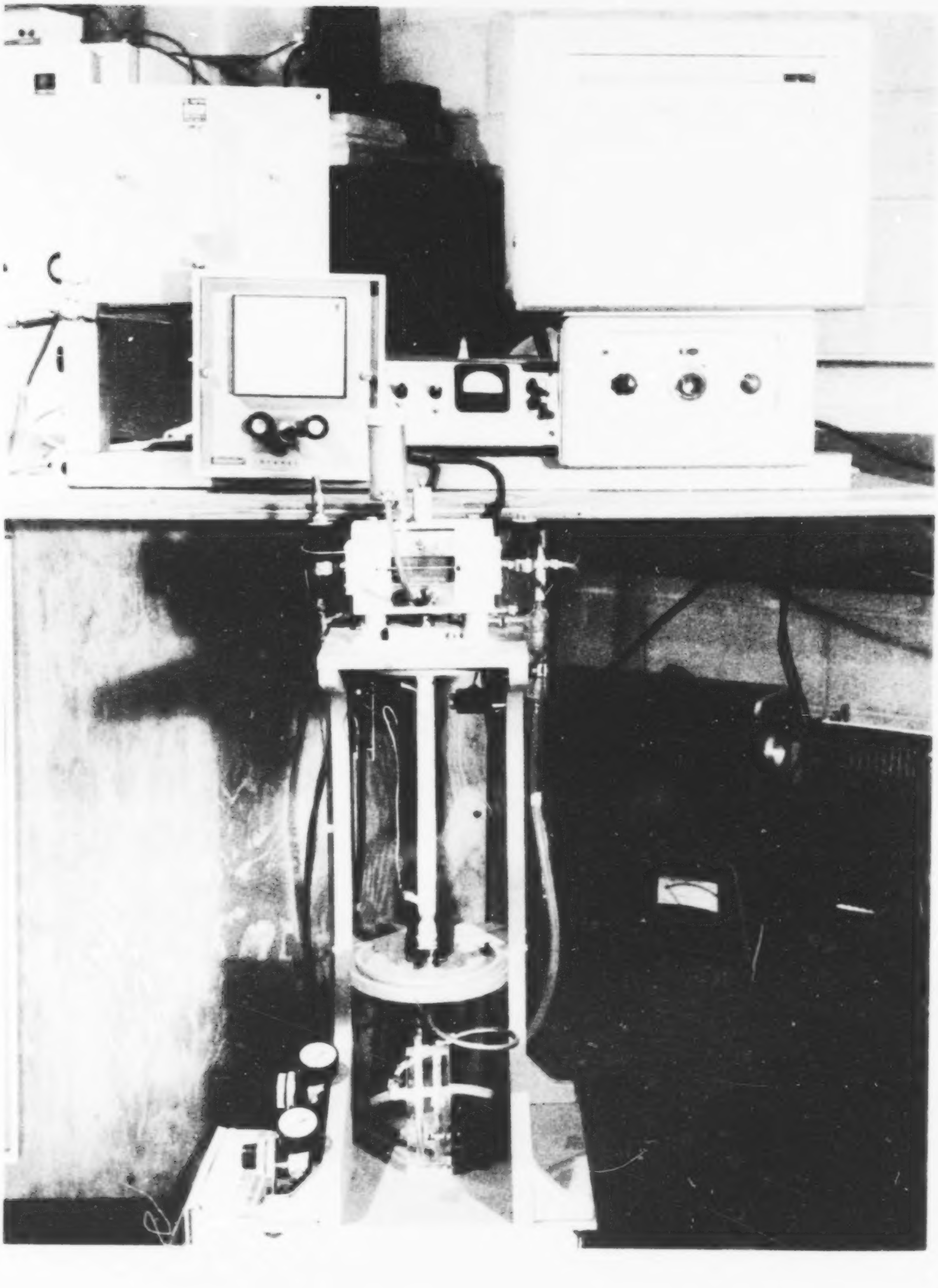
The tube was maintained at 800°C by a Palladium heating element. At this temperature, the organic compounds present in the waste stream were oxidized to CO_2 and water; the CO_2 liberated was proportional to the amount of carbon present in the sample. The gas stream was passed through a separator in which the water vapor was condensed and collected. The CO_2 and carried gas then passed through a Beckman model IR315 infrared analyzer, which was selective to CO_2. The output from the infrared analyzer section was recorded on an L & N model W strip chart recorder as a peak height similar to that from a gas chromatograph.

The Phoenix Varipump is a system which produces a constant volumetric flow rate with varying concentration of some components in the output stream. It consists of two small pumps which draw from two tanks at different concentrations of some component. The pumps are connected through a servomechanism to a photoelectric cell which follows a curve traced on a revolving drum. The cell follows the outline of the curve against a black background, and varies the flow rates of the two pumps so that the volumetric flow rate remains constant, while the concentration of the output stream varies according to the curve traced on the revolving drum.

The Beckman infrared analyzer was calibrated using samples of acetic acid-water solutions of different concentrations of organic carbon. Solutions of acetic acid in water containing 0, 10, 20, 40, 60, 80, and 100 ppm of organic carbon were prepared and run through the analyzer section. The output peak heights were recorded and a curve of peak height vs. total carbon was drawn and used as the standard for each run. Before each experimental run, the calibration curve was checked by running one or more of the standard samples through the analyzer to make sure that the previous calibration was still valid for that day. During any one run the sensitivity of the analyzer did not change appreciably, and the results of the analyzer were reproducible.




0 1 2 3 4 5 6 7 8 9 10



EXPERIMENTAL RESULTS OF ACID - BASE SYSTEM

Several experimental runs were made in the pH range of 5-9 to test the validity of the mathematical model which had been derived. A total of nine runs were made, three each at residence time of 98.6, 246.5, and 493.0 minutes. The pH of the feed solution was constant for all nine runs at 11.2. Figure 10 compares the experimental pH versus time curves with those predicted from the mathematical model using a total inorganic carbon concentration of o.75 ppm.

In general there is good agreement between the calculated and experimental results, indicating that the model is indeed the correct one. The greatest source of error in the experimental phase was the measurement of the total inorganic carbon concentration. Although the infrared analyzer measurers the total carbon accurately, it is difficult to distinguish between the organic and inorganic carbon concentrations.

The assumption that the reaction was completely mixed was also proven to be valid experimentally. A run was made with the CO_2-free water, thus eliminating any buffer effect due to the inorganic carbon. As shown in Figure 11, the experimental and calculated results fall on the same curve, proving that the system is indeed completely mixed.

EXPERIMENTAL RESULTS OF ACTIVATED SLUDGE SYSTEM

Several titrations of sludge solutions were made to determine the value of K_3 for activated sludge. Three 500-ml. samples were prepared with equal total solids concentration. The first sample was titrated at full strength. The second sample was filtered to remove the solids and combined with the third to give 1000 ml. of suspension with a total solids concentration equal to one half that of the original sample. This was then separated into two 500-ml. samples, one of which was titrated. The third sample was then separated into two 250-ml. portions, one portion was filtered to remove the solids and recombined with the other to give 500 ml. with total solids equal to one fourth of the original sample. This sample was also titrated. A fourth sample of the same solution was filtered to remove all the solids and titrated as a blank, or reference sample.

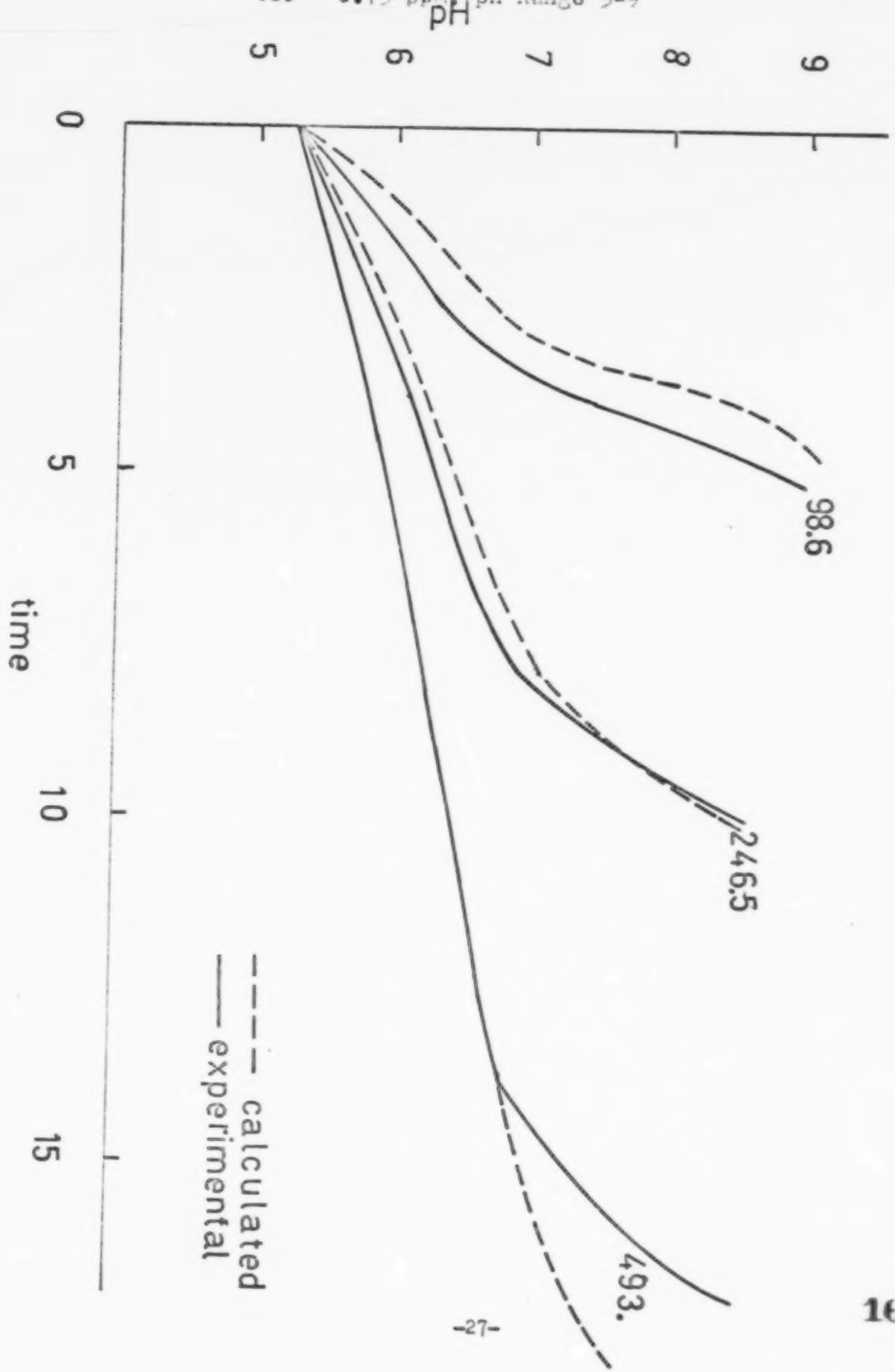
As shown in Figure 12, a plot of pH versus equivalents of H^+ added, there is an effect on the amount of acid required to reach a particular pH due to the sludge concentration. As the concentration increases, so does the amount of acid required. Figure 13 is a plot of the normalized function Δ/TS for the three samples. Within the limits of experimental error, the normalized function is practically independent of total solids concentration. Calculations to obtain K_3 from the normalized curves gave values of $pK_3 = -2.95, -2.80$, and -2.85 for samples 1, 2, and 3 respectively. Therefore, the experimental value of pK_3 would be the average of the three, -2.80, and $K_3 = 710$.

One major difficulty was experienced with the experimental equipment which rendered the data taken for the activated sludge system useless. The continuous centrifuge was unable to filter the sludge effectively from the reactor effluent. This caused gross inaccuracy in the total carbon data, since the measurements consisted of both suspended solids and dissolved carbonaceous material, the separate amounts of which could not be determined.

ACKNOWLEDGMENTS

This project was supported in part by a Water Supply and Pollution Control Demonstration Grant No. WPD-175-02-68 from the U. S. Public Health Service.

Figure 10 - Experimental and Calculated Plots of pH as a Function of Time with Residence Time as a Parameter, TIC = 0.75 ppm, pH Range 5-9



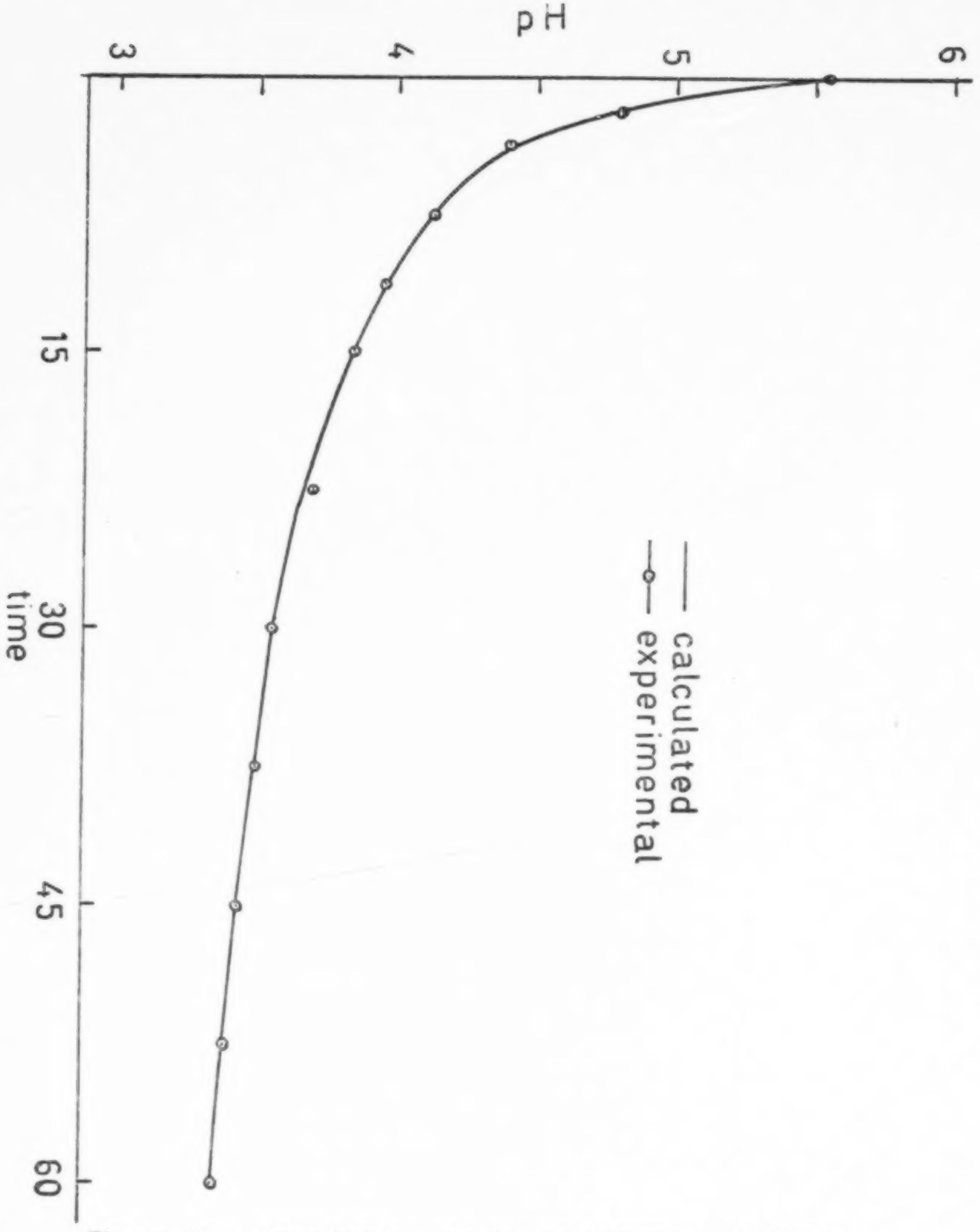


Figure 11 - Experimental and Calculated Plots of pH as a Function of Time, TIC = 0 ppm, 98.6 Minutes Residence Time

Figure 12 - pH Versus Milliequivalents of H^+

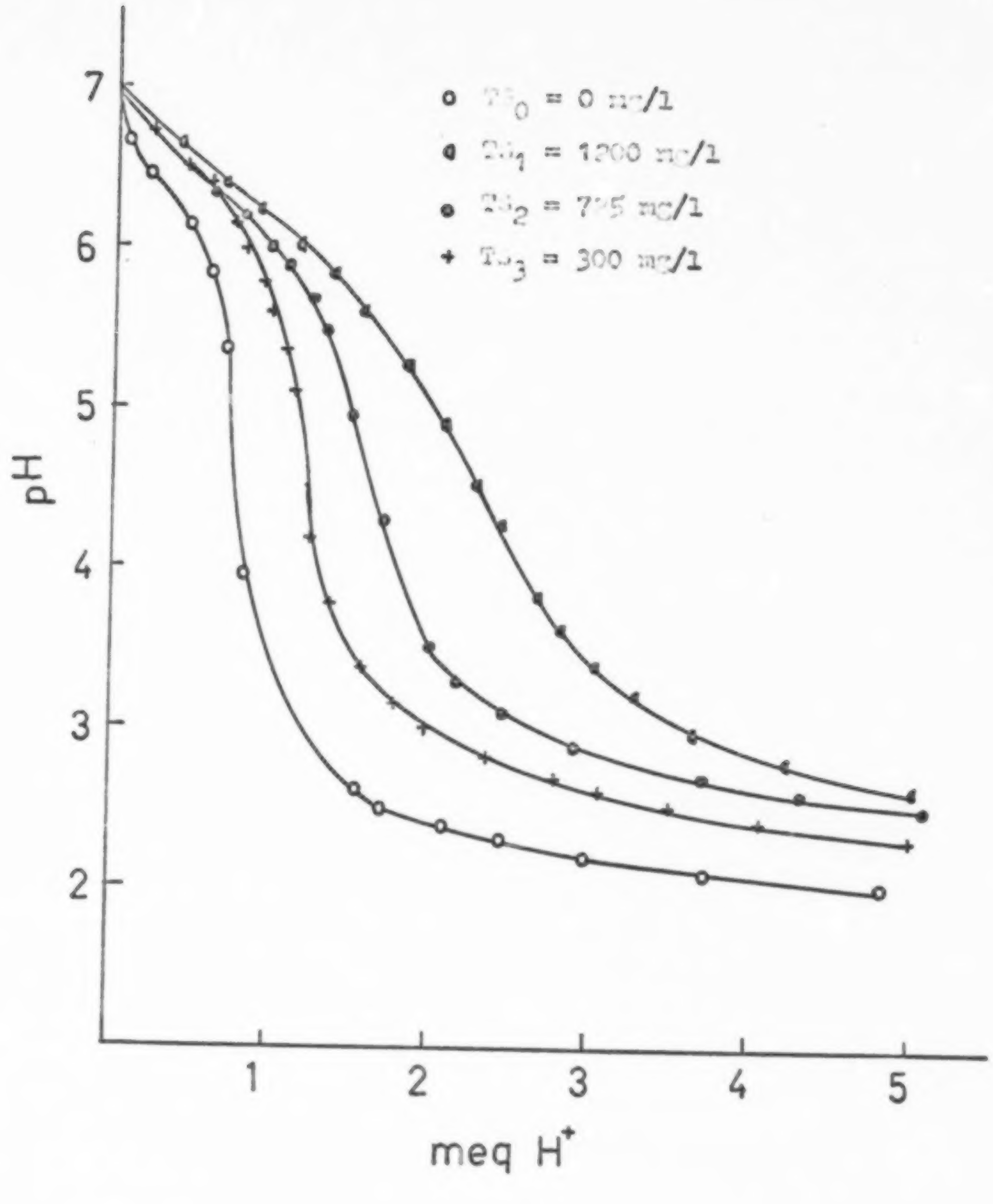
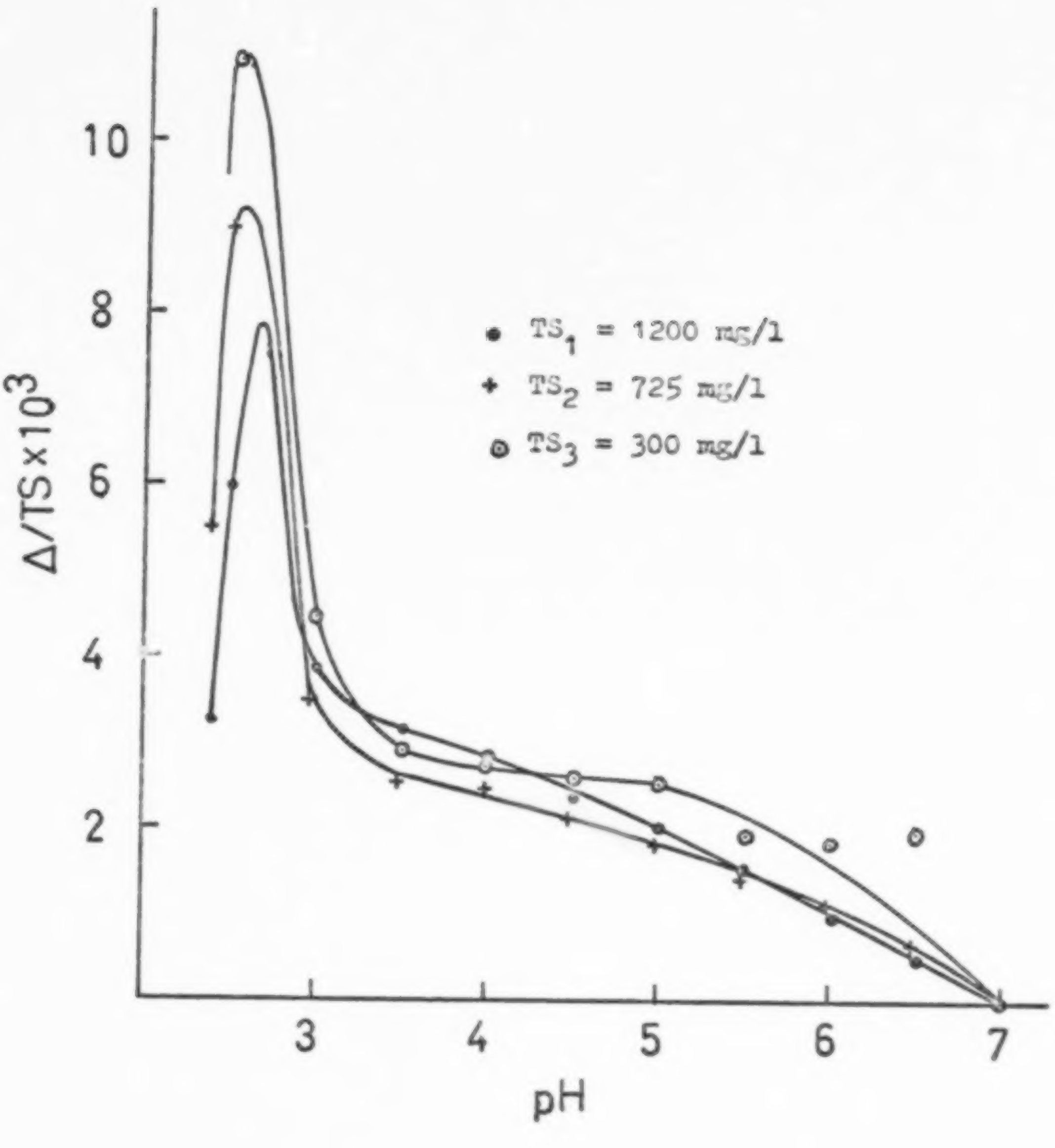


Figure 13 - Normalized Function, Δ/TS, Versus pH



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DETERMINATION OF MIXING IN A GAS SPARGED REACTOR

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SUMMARY

The purpose of this project is to determine under what conditions complete mixing can be attained in a gas sparged reactor. The immediate application of gas sparged reactors is in the activated sludge waste water treatment process. The axial dispersion coefficient, D_L, which provides a measure of the degree of mixing during flow was determined from a pulse tracer injection of a known concentration of NaCl solution. The dispersion coefficient was correlated in terms of a Peclet Number, $\frac{U_L d_t}{D_L}$, based on liquid flow velocity and tube diameter. The Peclet Number was calculated from residence time distribution data involving the statistical variance from the solution to the differential diffusion model equation. A six inch diameter Pyrex column was used as the reactor. The water flow rate and the air rate were varied for different length to diameter (L/d_t) ratios of the column. The tracer output concentration was measured using a conductivity cell and was recorded dontinuously over the time interval for each experimental run.

The reactor was found to be essentially completely mixed for superficial gas velocity greater than 0.03 ft/sec. For gas velocities greater than 0.03 ft/sec., the following generalized correlation was found:

$$Pe = \frac{U_L d_t}{D_L} = 2.80\,(Ug)^{-.118}(L/d_t)^{-.976}$$

INTRODUCTION

The objective of any mixing process is homogenization. Mixing is undertaken in order to attain an intimate mutual distribution of the constituent materials. Perfect mixing of several components may be defined as the state in which infinitesimal volumes of the mixture withdrawn from any point within the system exhibit the same composition. Rapid mixing necessitates motion of the constituent materials of the system. The method for setting the material in motion and maintaining it in this state is influenced by the properties of the material which largely determine the nature of the mixture. The fundamental requirement of mixing is motion of the materials to be mixed. This motion may occur spontaneously or by forced mixing.[1]

Spontaneous mixing is a slow process. The attainment of faster mixing than is effected by spontaneous processes requires forced mixing which is attained by efficient motion of the fluid, or in other words, flow. The immediate application of complete forced mixing in a gas sparged reactor is the activated sludge waste water treatment process for domestic sewage. The completely mixed activated sludge process requires instantaneous mixing of incoming air with untreated water through the entire aeration tank. This is necessary so that organic load on the aeration tank is uniform from one end to the other end and so that a uniform oxygen demand and a uniform biological growth is produced. This aeration tank then has the opportunity to operate as a surge tank to level out variation in the organic strength of the raw waste so that shock loads due to variation in the concentration of organics do not have a shock effect on the microorganisms in the aeration tank.[2]

The axial dispersion coefficient D_L provides a measure of the degree of mixing. Complete mixing implies that D_L approaches infinity (∞). Therefore, for a gas sparged unit as $D_L \rightarrow \infty$, $Pe = U_L d_t / D_L \rightarrow 0$. The Peclet Number varies from infinity for a plug flow reactor to zero in magnitude for a complete backmixed reactor. A decrease in the Peclet Number corresponds to a rise in the degree of mixing.

PREVIOUS WORK

Several studies have been done on mixing in sparged reactors.[3, 8, 9] However, previous studies have been directed at obtaining qualitative effects rather than general equations suitable for design. Argo and Cova[3] have carried out gas-sparged longitudinal mixing experiments on several systems. They injected a tracer at a constant rate of flow into a continuously flowing reactor with the gas feed and tracer injection point at the same position. They made a measurement of the steady state concentration gradient of tracer at a point downstream from the injection point. From their steady-state mathematical model solution, they calculated dispersion coefficients from the experimental data. They plotted dispersion coefficients versus superficial gas velocities. For their gas-water system their turbulent regime begins at superficial gas velocities of about 0.167 ft/sec. It is characterized by agglomeration of bubbles. But this is not to be misunderstood that complete mixing occurs at the onset of the turbulent region. This can be seen from the report of Fair[4] where a plot of a modified Peclet Number versus superficial gas velocity indicates a Peclet Number starting to approach zero at superficial gas velocities of 0.30 ft/sec.

The data of Argo and Cova were replotted in Figure 1 as Peclet Number ($\frac{U_L d_t}{D_L}$) in terms of liquid velocity U_L, and tube diameter d_t versus Superficial Gas Velocity U_g. If a better knowledge of the effects of L/d_t (length of non-aerated liquid section of tube over the tube diameter) were known, the significance of this might also have been shown on the plot in Figure 1. But the data available seems to indicate that at high superficial gas velocity, the better mixing is attained. The objective of this project is to check Pe as $U_g \rightarrow 0$ and the effect of L/d_t.

THEORY

The general representation of the dispersion model which mathematically describes the system is

$$\frac{\partial C}{\partial \theta} + \nabla \, (\underline{U}_L C) = \nabla \cdot (\underline{D} \nabla C) + r_c$$

where C is the observed liquid phase tracer concentration,

r_c is the generation term for chemical reaction

$\underline{D}$ is the dispersion coefficient tensor

$\underline{U}_L$ is the liquid phase velocity

θ is the time variable

The dispersion coefficient or diffusivity is, in general, a function of both the fluid properties and the flow situation and is nonisotropic, or in other words, it has different values in different directions. Therefore, the coefficient may be represented by a second order tensor, and if the principal axes are taken to correspond with the coordinate system, the tensor will consist of only the diagonal elements. Since the system to be studied is for cylindrical flow, and with the following simplifying assumptions:

a) constant density, $\nabla \cdot \underline{U}_L = 0$

b) bulk flow in the axial direction only

c) radial symmetry, for this the dispersion coefficient tensor reduces to:

$$\underline{D} = \begin{pmatrix} D_L(r) & 0 & 0 \\ 0 & D_r(r) & 0 \\ 0 & 0 & D_r(r) \end{pmatrix}$$

d) no chemical reaction, $r_c = 0$

the general equation in cylindrical coordinated reduces to

$$\frac{\partial C}{\partial \theta} + U_L(r) \frac{\partial C}{dx} = \frac{\partial}{dx} D_L(r) \frac{\partial C}{dx} + \frac{1}{r} \frac{\partial}{\partial r} r \, D_r(r) \frac{\partial C}{\partial r}$$

The solution of the above equation is extremely difficult. To permit an analytical solution, the following further simplifying assumptions are made:

e) dispersion coefficients are independent of position and the fluid is flowing at the mean velocity

$D_L(r) \quad = D_L$

$D_r(r) \quad = D_r$

$U_L(r) \quad = U_L$

f) no variation in properties in the radial direction, $\partial C/\partial r = 0$, the above equation reduces to[5]

$$\frac{\partial C}{\partial \theta} + U_L \frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial x^2}$$

If $Z = x - U_L\theta$

and $\theta = \theta$

then

$$D_L \frac{\partial^2 C}{\partial Z^2} = \frac{\partial C}{\partial \theta}$$

The boundary conditions for the problem are:

a) $C(Z,0) = 0$ for all $Z \neq 0$

b) $C(0,\theta\ ) = \delta(0)$ at $\theta = 0^+$, delta impulse of zero thickness

$\lim\limits_{Z \to \infty} C(Z,\theta\ ) = 0$

c) $Q = \frac{\pi r^2 L}{L} \int_{\infty}^{\infty} C(Z,\theta)\, \partial Z$

where Q is the volume of tracer injected at $x = 0$ across a tube of volume $V = \pi\ r^2 L$ and length L[6].

The solution to the above equation with boundary conditions given for a fluid flowing at v ft^3/sec. which enters an experimental section of a column of volume V ft^3 at $x = 0$ and $\theta = 0$ and leaves at $x = L$ and where the slug of tracer moves downstream at an average velocity $U_L = vL/V$ ft/sec. is given by

$$C = \frac{Q\, L}{2V\sqrt{\pi\, D_L\, \theta}} \quad \exp \; - \frac{(x-U_L\theta)^2}{4\, D_L\theta}$$

The variance, σ^2, for this output has been found[7, 10] to be

$$\sigma^2 = 8\left(\frac{D_L}{U_L L}\right)^2 + 2\left(\frac{D_L}{U_L L}\right)$$

or solving for $D_L/U_L L$ yields

$$\frac{D_L}{U_L L} = \frac{1}{8} \quad \left(\sqrt{8\,\sigma^2 + 1} \; - 1\right)$$

which is a reciprocal Peclet Number defined in terms of column length L and liquid velocity U_L. A value of D_L can be determined from the above equation if the variance σ^2 is known. It should be emphasized, however, that this variance refers only to the model and such cases where the model perfectly describes the physical situation.

In practice the variance of the experimental data will be measured and the data will be "fit" to the model by assuming that

$$\sigma^2 \text{ data} = \sigma^2 \text{ model}$$

The variance expression for the time-concentration data is modified by replacing the integrals by finite sums and by replacing the theoretical function CV/Q by the observed concentration readings. The modified formula then is written as

$$\sigma^2 = \frac{\Sigma x^2 f}{\Sigma f} - \left(\frac{\Sigma x f}{\Sigma f}\right)^2$$

where x corresponds to θ, f corresponds to or is proportional to CV/Q (arbitrary concentration units) and the summation is taken over all the time readings.[7] Therefore, with the data obtained, Pe can be found from

$$\frac{U_L d_t}{D_L} = \frac{d_t}{L} \quad \frac{1}{\frac{1}{8}\sqrt{8\sigma^2 + 1} \; - 1}$$

PROCEDURE

EXPERIMENTAL: GENERAL OPERATION PROCEDURE

The system which was used is shown in Figure 2. The reactor diameter was 4", 6", and 12". The liquid level was varied with these reactors to give a range of L/d ratios. The water inlet was located at the bottom of the column as shown in Figure 2. The water was removed from the upper portion of the column by use of a pump which drew the water-salt solution through the conductivity cell first and then through the pump and into the disposal area. A continuous record of the concentration of the solution was kept on a strip chart recorder.

Three different liquid flow rates of 0.459 gal/min, 0.2295 gal/min, and 0.11475 gal/min were run at those particular steady state L/d_t ratios. For each liquid flow rate and L/d_t ratio, seven different superficial gas velocity of 0, 0.0171, 0.0342, 0.0513, 0.113, 0.188, and 0.420 ft/sec were bubbled through the water. At time zero, a certain amount of tracer was injected. The output concentration reached the preinjection level.

Tracer System

The tracer flow system consisted of an injection device, an injection point and a sampling point. A

$$\frac{2.7 \text{ gr NaCl}}{40 \text{ ml } H_2O} = .0675 \text{ gm/ml}$$

solution of sodium chloride was chosen for the tracer mainly because it had a linear relationship of conductivity and concentration over a much wider range of concentration than was actually needed. For each different level of liquid height, a different volume of tracer was injected so as not to exceed the maximum conductivity of 500 micromhos on the conductivity meter. All injections were made through a 14-gage needle which was inserted permanently and partially into the inlet water line a short distance before the experimental section under observation. When the tracer was not being injected, the needle was closed by pinching a short section of rubber tubing in the 14-gage injection needle. The solution leaving the top of the column was pumped through a conductivity cell with temperature compensation. The solution was then discharged at the outlet of the pump which provided the withdrawal power for the system. The small lag time between the top of the liquid in the container and the conductivity cell was taken into account in the calculation.

Sparger Unit

The sparger base for the system is shown in Figure 3. The base was machined from brass hexagonal bar stock. The sparger arms were machined from 3/8" diameter brass stock. Six arms of appropriate length to just fit in the column were bored out leaving a seal at the unthreaded end. Holes of 3/32" diameter were drilled and placed along the bottom of each arm in order that the superficial gas velocity, U_G, be $\leq$ 0.4 ft/sec, and the nozzle velocity be $\leq$ 10 ft/sec.

Measuring System

The measuring system consisted of a flow-through conductivity cell, a continuous reading conductivity meter, a temperature compensator, and a recorder.

The flow-through conductivity cell was a Beckman CEL-II(33)M1, platinized nickel electrode with an alumina electrode holder and a phenolic rubber shield. The cell constant was 1.0/cm which gave a range of 0 to 500 micromhos/cm. The conductivity meter was a Beckman RA5 Direct Reading Conductivity Meter (Solu Meter).

The temperature compensator was a Beckman T1C-MT which controlled the output of the AC milliammeter to provide the correct conductance indication over a temperature range of 32-122° F for the NaCl electrolyte being measured. This automatic temperature compensator provides a maximum error equivalent to a departure of no more than 1° F or usually above 1.5% from the electrolyte characteristic curve.

Even though the meter deflection was essentially instantaneous and easily read, the rapidity of the pulse required a continuous recording of conductivity. The recorder was an Esterline Angus Model E1101E with a 0-1- millivolt DC signal to coincide with the Solu Meter signal.

ANALYTICAL

The strip chart recordings of concentration in terms conductivity versus time are analyzed to obtain the variance σ^2 of each curve. For each experimental run the conductivity of the outlet is allowed to reach as closely as possible the baseline established at the outset of the run so that the analysis of the curve gives an accurate value of variance for that curve.

The variance, σ^2, of the curve is

$$\sigma_\theta^2 = \frac{\Sigma x^2 f}{\Sigma f} - \left(\frac{\Sigma xf}{\Sigma f}\right)^2$$

where σ_θ^2 is in terms of sec^2

x is the time reading from off the curve

f is the arbitrary concentration unit from off the curve corresponding to the time value

σ^2 is converted to σ^2 for use in the formula for determining D/UL by the following relationship:

$$\sigma^2 = \sigma_\theta^2 / \theta^2$$

where θ is the residence of a particular test section and is adjusted so as to consider the lag time resulting from the measuring tube section in front of the conductivity cell. Values of time and concentration units were taken from each graph with the concentration units being corrected to a zero established baseline by subtraction of the baseline reading from the actual reading. An IBM 1620 computer program was written to facilitate the calculation of σ_θ^2 by the square of residence time for each run. $D_L/U_L L$ is then calculated from the formula developed previously, which was

$$D_L/U_L L = \frac{1}{8} \left(\sqrt{8 \sigma^2 + 1} - 1\right)$$

$D/U_L L$ was then multiplied by L/d_t and the reciprocal of that result was taken to give the desired Peclet Number, $U_L d_t/D_L$, in terms of tube diameter, d_t. The Peclet Number was then plotted versus superficial gas velocity Ug with L/d_t as a parameter for each liquid flow rate. Figures 4, 5, and 6 show the Peclet Number versus superficial gas velocity, Ug, for various ratios of L/d_t.

All the data above the superficial gas velocity of 0.0342 ft/sec were correlated in a general plot of the following form:

$$Pe = k \, (Ug)^{\alpha} \, (L/d_t)^{\beta}$$

In terms of natural logs the above equation is

$$\ln Pe = \ln k + \alpha \ln Ug + \beta \ln L/d_t$$

The equation was then rearranged as

$$\ln Pe - \alpha \ln Ug = \ln k + \beta \ln L/d_t$$

and the data were plotted on long-log paper as

$$Pe/Ug^{\alpha} \quad \text{vs} \quad L/d_t$$

with k as the ordinate intercept at $L/d_t = 1.0$, and β as the slope of the straight line. To fit the data to a straight line of this sort, a least square analysis was performed on the 1620 computer. Figure 7 in the Results section shows the plot of the data and the straight line correlation obtained by the least squares fit.

Figure 8 in the Appendix shows a typical concentration versus time curve for a particular experimental run, labeled EE. The run shown was for an L/d_t ratio of 5.34 with a superficial gas velocity of 0.113 ft/sec and liquid flow rate of 0.2295 gal/min. Concentration in terms of conductivity at various time intervals was taken for this and similar curves to determine the data variance σ_{θ}^2.

On the same figure the complete mixing and plug flow curves are also shown.

DISCUSSION OF RESULTS AND CONCLUSIONS

Each set of curves shows a change in the incidence of complete mixing with liquid flow rate. This change occurred at superficial gas velocities of about 0.0342 ft/sec, 0.09 ft/sec, and 0.18 ft/sec for liquid flow rates of 0.459 gal/min, 0.2295 gal/min, and 0.11475 gal/min, respectively. It must be emphasized that these points are just incidences of complete mixing since the systems are not completely mixed unless Pe = 0. For superficial gas velocities above this incidence point, the mixing is not controlled by the bulk flow but rather by the forcing of air through the experimental section which gives rise to forced diffusion transport. This is borne out by the qualitative definition of the Peclet Number which is a ratio of

$$\frac{\text{Bulk mass transport}}{\text{Diffusive mass transport}}$$

If the liquid flow were plus flow, there would be no y-intercept at zero gas velocity since the Peclet Number approaches infinity. For the liquid flow rates used, fully developed laminar flow was achieved. The equation used to determine the length L downstream from the entrance of the column where the laminar boundary layer was fully developed was

$$\delta = 5.0 \sqrt{\frac{\nu L_a}{U_o}}$$

where $\nu = \mu / \rho$, the kinematic viscosity

U_o = velocity of water at the entrance

L_a = length downstream for fully developed laminar flow

δ = boundary layer thickness

For all cases fully developed laminar flow was achieved at the measuring point of each exit system and gives rise to a y-intercept.

In the region past the incidence of complete mixing, a terminal mixing point seems to be reached. The completeness of mixing is achieved by the amount of liquid-gas interfacial contact. As one increases the superficial gas velocity, more air is pushed through the system. This additional air does not form more bubbles as before but rather makes the bubbles largerin order to handle the increased gas flow. Since additional (surface area)/cubic ft minute of gas) is lower in this latter case, the effect of the higher gas rates on mixing also is lower.

The ordering of the curves at zero superficial gas velocity, that is, higher Peclet Numbers as L/d_t decreases is explained by considering the fluid flow velocity patterns. As L/d_t decreases, one get closer to the entrance section of a conduit where the velocity profile is not nearly as developed as it is at greater distances from the entrance. Therefore, plug flow is more nearly approached which gives rise to less mixing by bulk flow and therefore lower dispersion coefficients and larger Peclet Numbers as the plot results indicate.

In general, the ordering of the curves for the various L/d_t is opposite of what one would expect. Ordinarily at high gas velocities for larger L/d_t ratios one would expect the air to break up the laminar profile to a more plug flow like pattern. This would then give rise to higher Peclet Numbers instead of lower ones. This conflict with our data may be explained by the fact that the operating range of the column length was short, therefore bringing in the entrance effects of the column into a more predominant role.

By comparing the relative position of the curves in Figures 4, 5, and 6, at a constant L/d_t for various liquid flow rates, one observes that the curve for the highest liquid flow falls below the other two instead of following a seemingly developed pattern of lying above the others. An explanation for this is that at the largest liquid flow rate, greater mixing is attained and therefore

D_L increases much more rapidly than the velocity of the liquid rises. This causes the Peclet Number which has the ratio $U_L d_t/D_L$ to decrease rather than increase.

Figure 7 shows the results of the generalized correlation

$$Pe = k(Ug)^{\alpha} (L/d_t)^{\beta}$$

where the constants were determined by a least squares fit and are

$$k = 2.80$$

$$\alpha = -.118$$

$$\beta = -.976$$

The values of these parameters indicate a slight dependence upon the superficial gas velocity and a strong dependence upon the L/d_t ratio. The small Ug dependence may be explained by the fact that a terminal mixing point is reached. The larger L/d_t dependence is explained by the fact that the experimental operation took place near the entrance section of the column.

ACKNOWLEDGMENT

Acknowledgment is made to the Federal Water Pollution Control Administration (Contract No. WPD-175-01-67) which provided the funds necessary to support the major portion of this study, and to the University of Connecticut Computer Center, which provided time on its IBM 1620 computer to analyze data.

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APPENDIX B

Figure 1 - Replotted Data of Arco & Cova

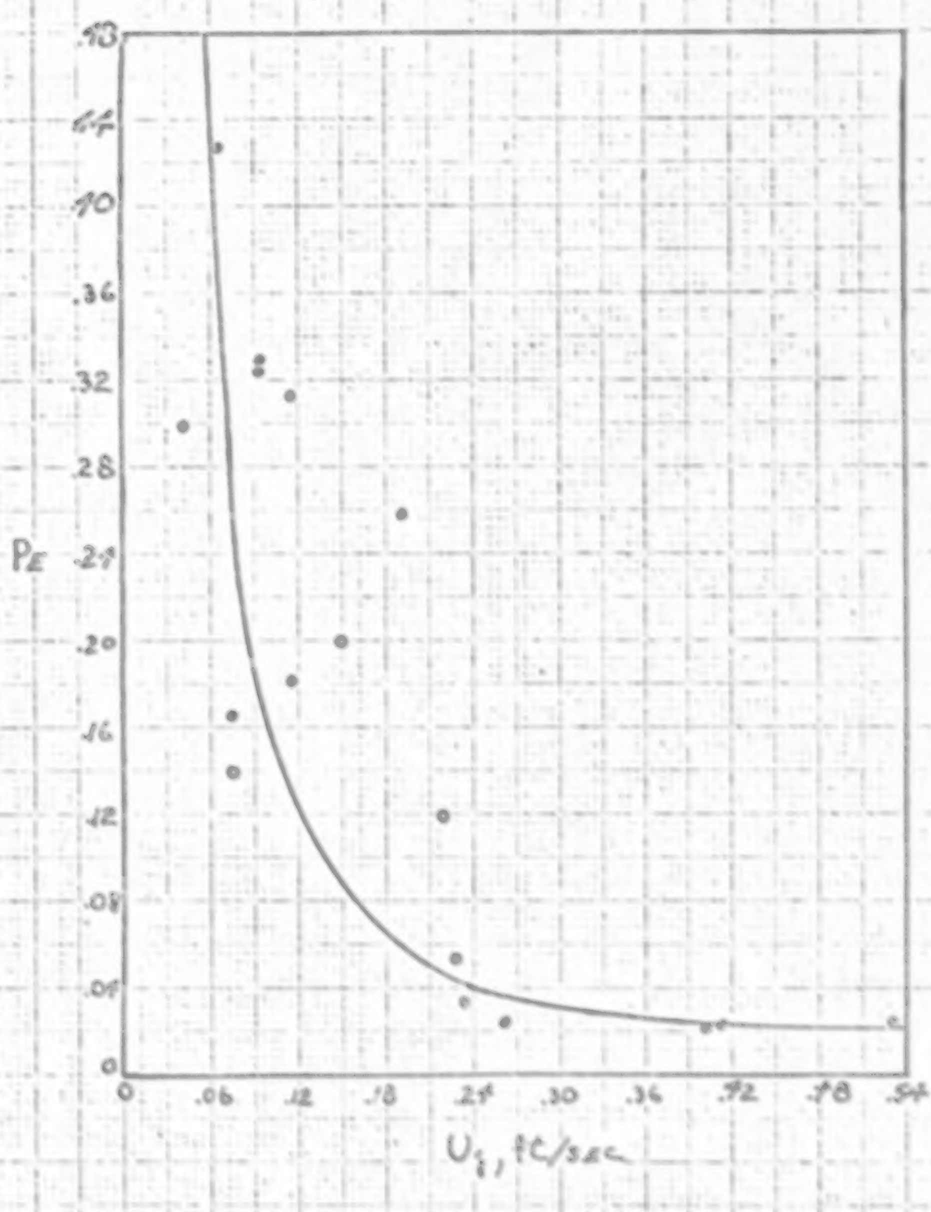


Figure 2 - Flow Sheet of Experimental System

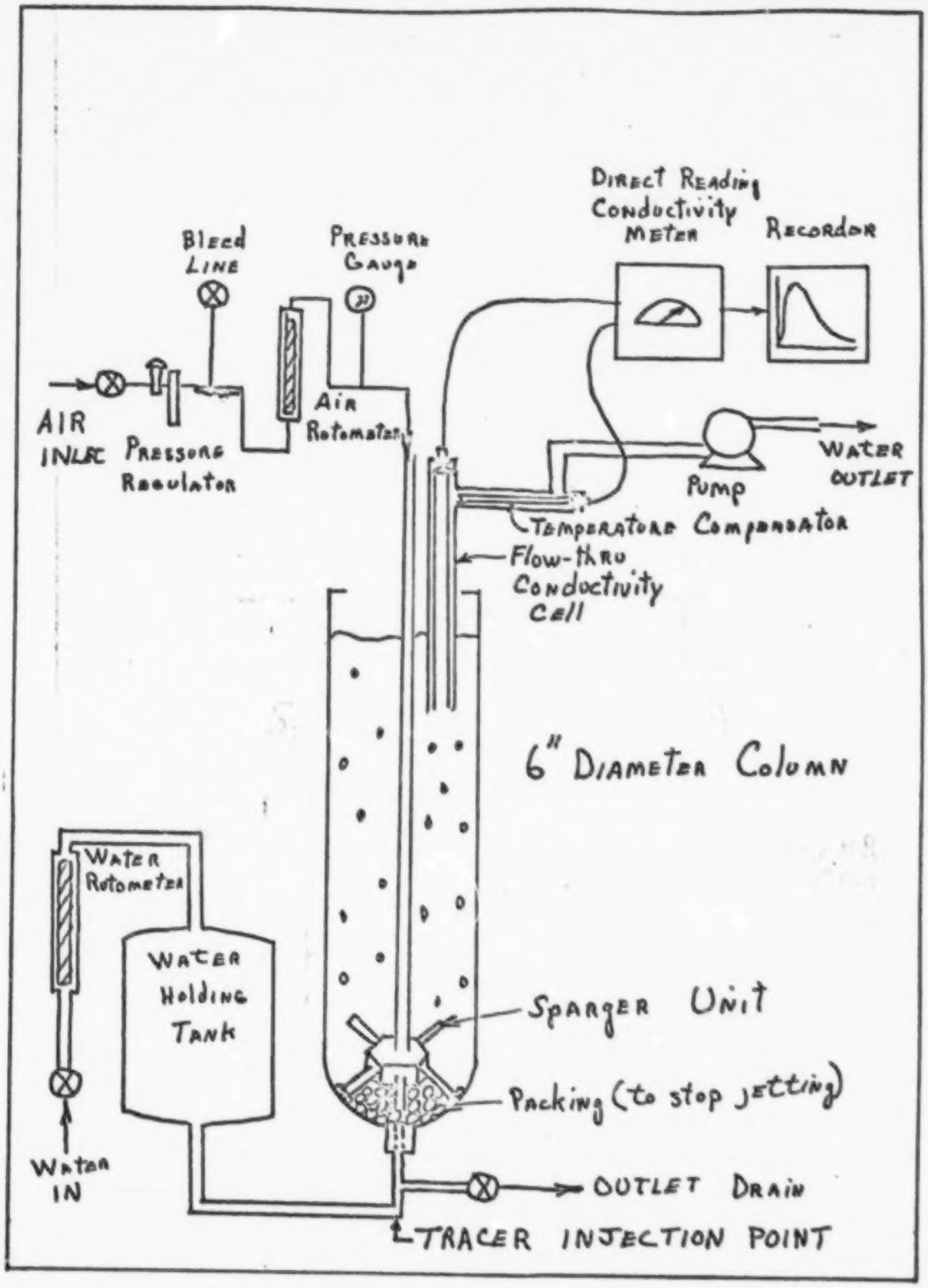
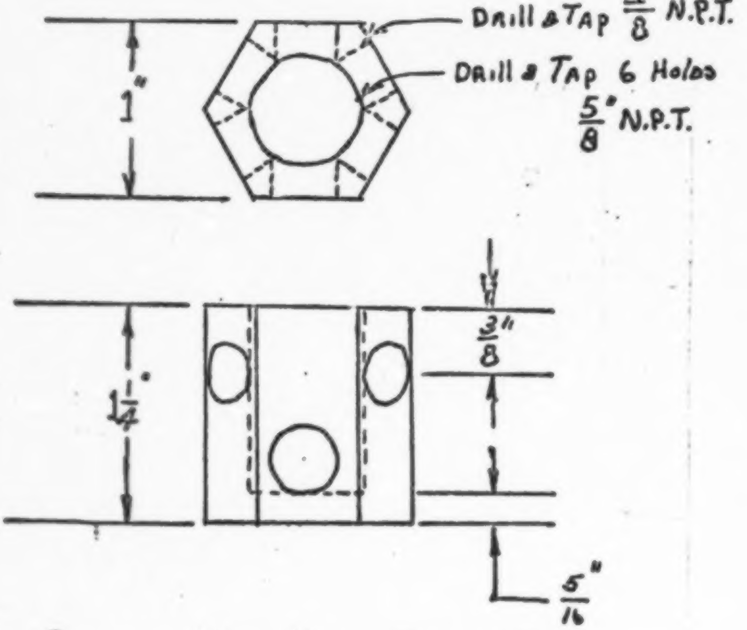
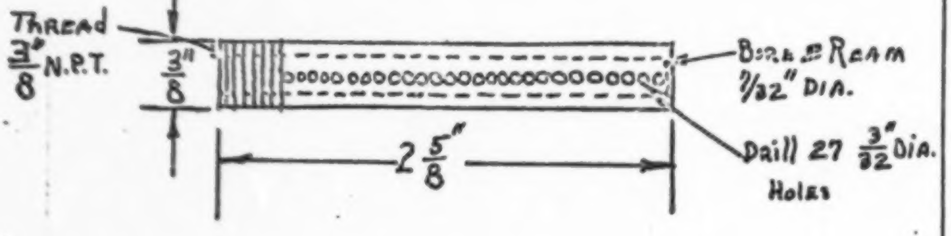

Direct Reading
Conductivity
Meter
Recorder
Bleed
Line
Pressure
Gauge
AIR
INLET
Pressure
Regulator
Air
Rotometer
Water
Outlet
Pump
Temperature Compensator
Flow-thru
Conductivity
Cell
6" Diameter Column
Water
Rotometer
Water
Holding
Tank
Sparger Unit
Packing (to stop jetting)
Water
IN
OUTLET Drain
TRACER INJECTION POINT

FIGURE 3

SPARGER BASE DESIGN


Drill & Tap 3/8" N.P.T.
Drill & Tap 6 Holes 5/8" N.P.T.
1"
1 1/4"
3/8"
5/16"

SPARGER HEX HEAD BRASS BASE


Thread 3/8" N.P.T.
3/8"
Bore & Ream 7/32" Dia.
Drill 27 3/32" Dia. Holes
2 5/8"

SPARGER ARM

Figure 4 - Plot of P_E against U_g for $w = 0.159$ Gal/min

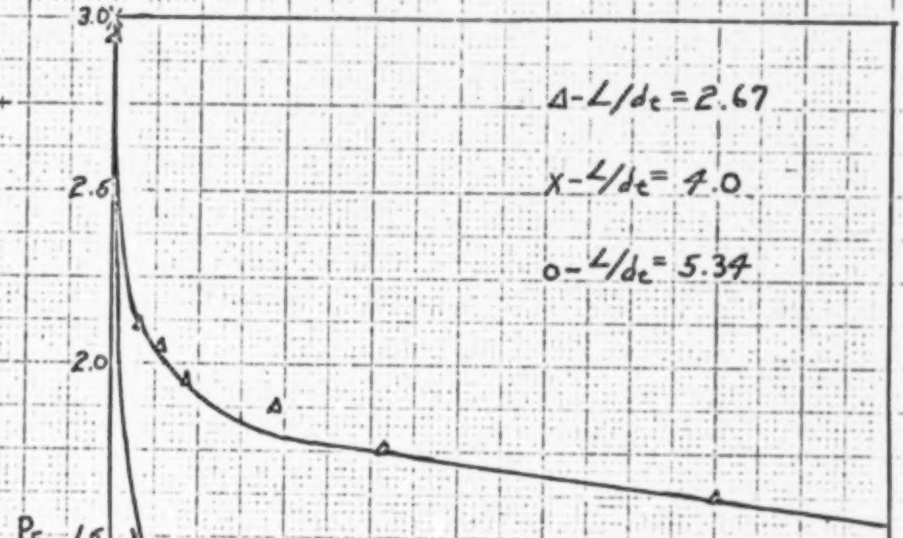


FIGURE 5 - Plot of P_E against U_j for $w = 0.2295$ Gal/min

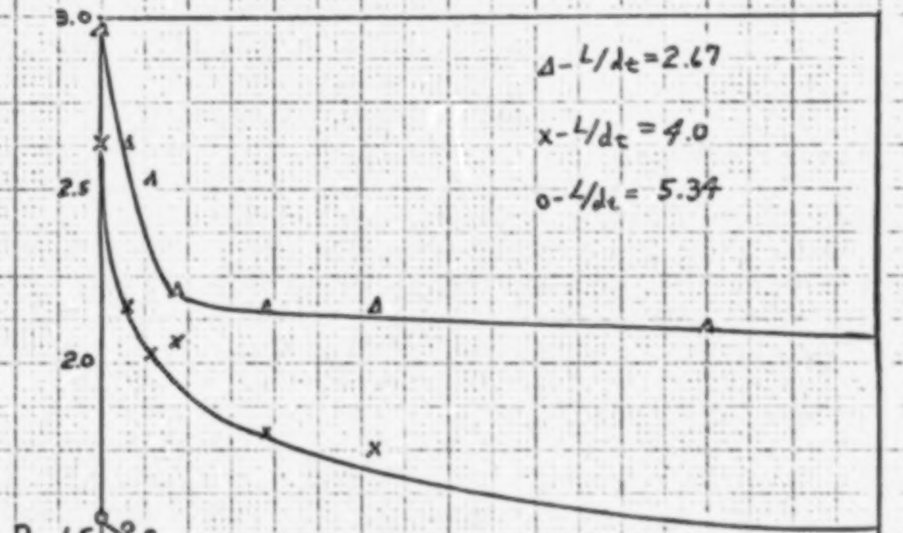
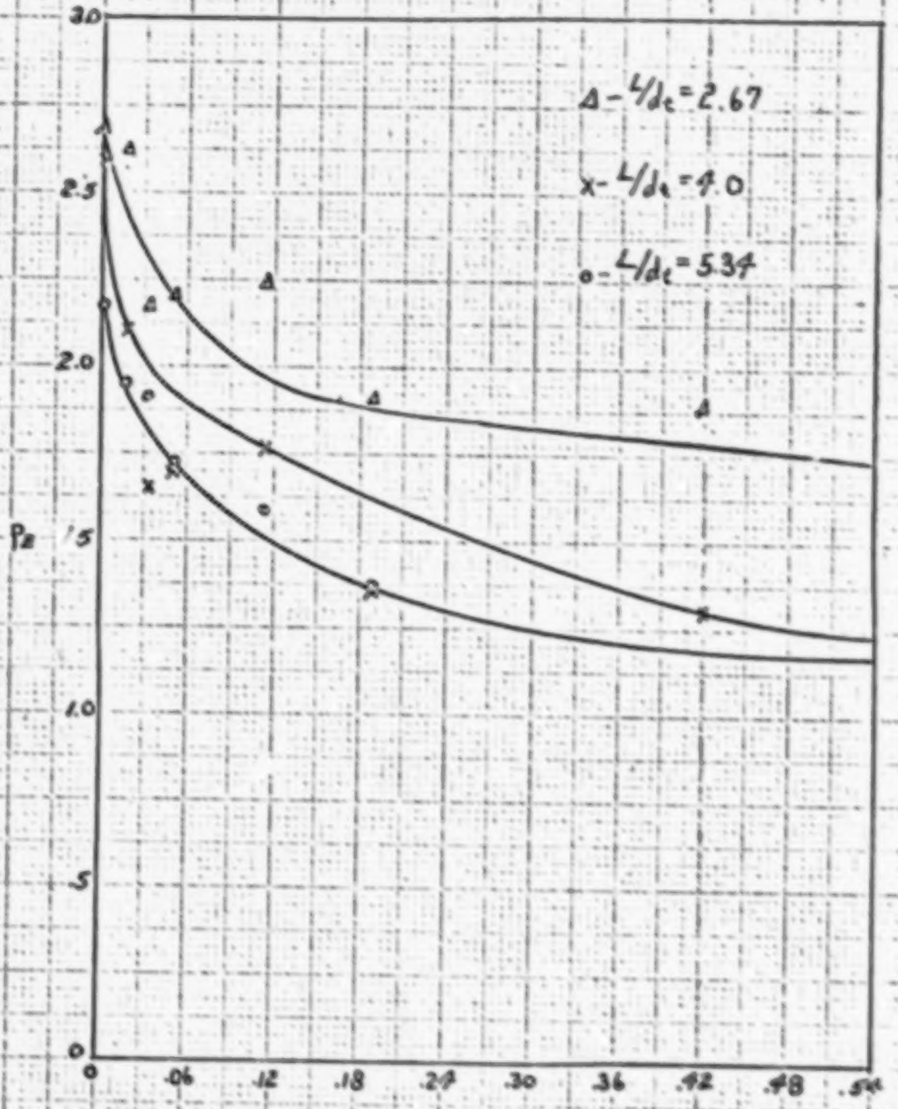


Figure 6 - Plot of P_2 against U_g for w = 0.11475 Gal/min



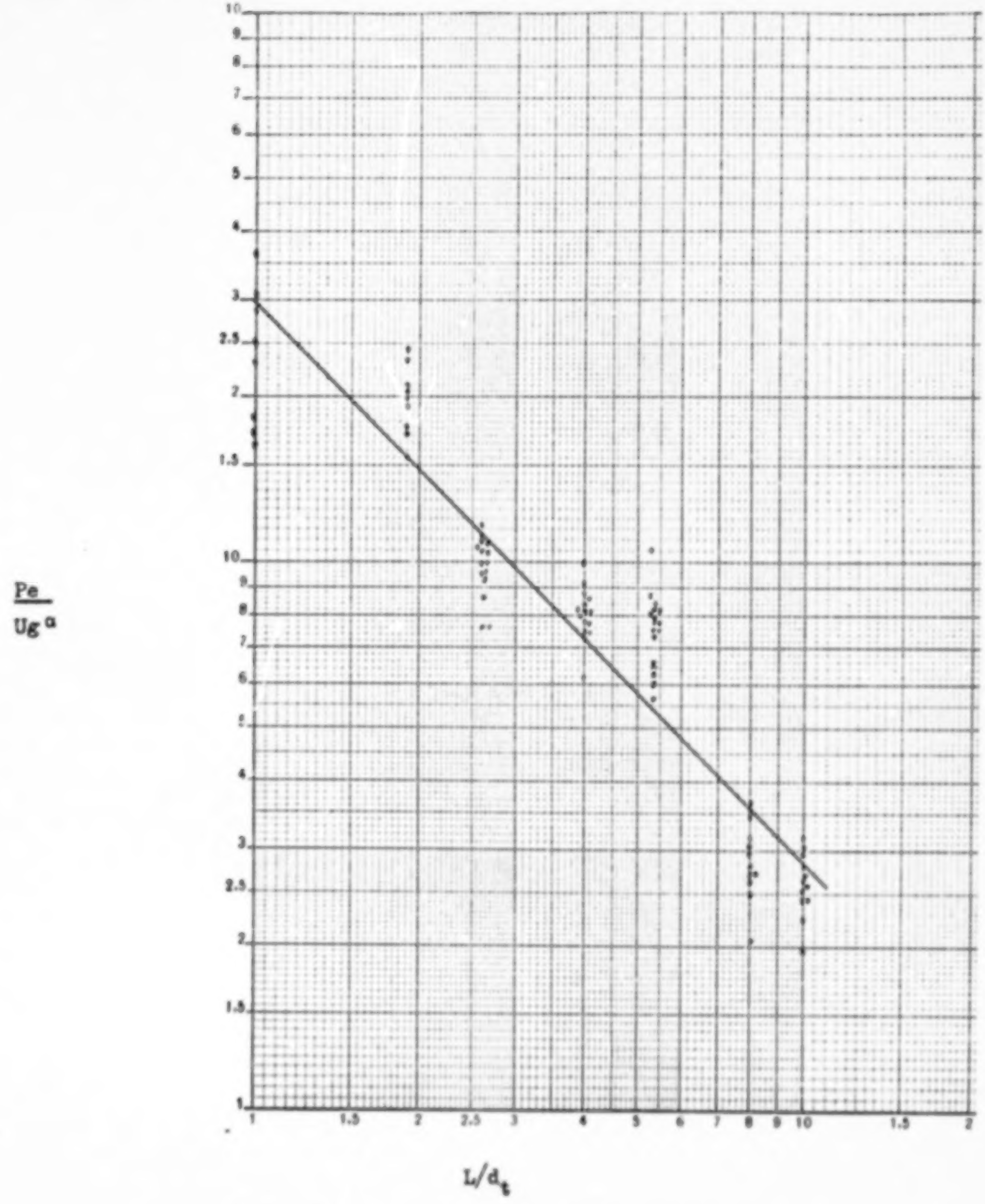
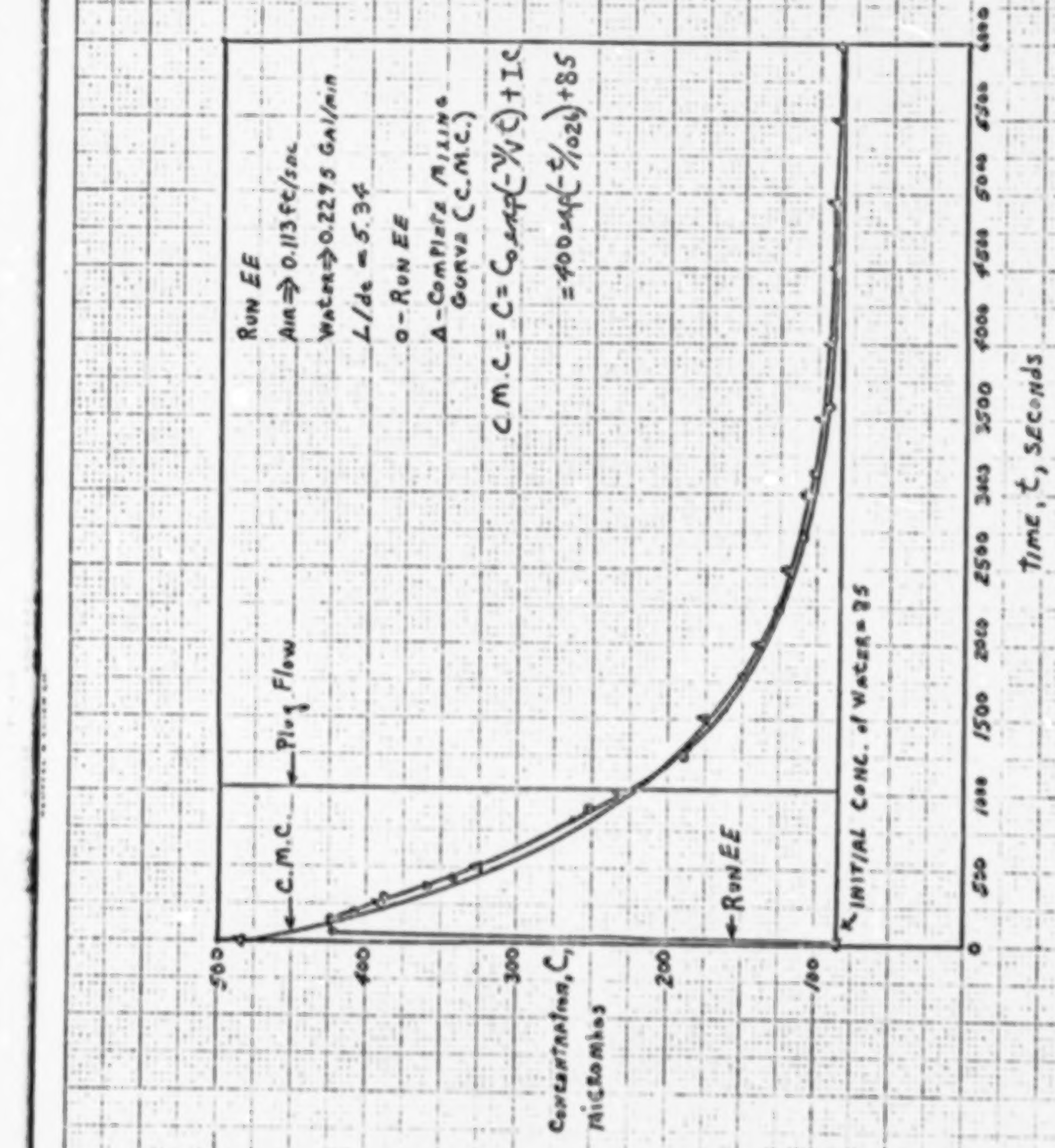


Figure 7. Generalized Correlation of Data

Figure 8 - Typical Concentration-Time Curve



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RESPONSE AND STABILITY OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR

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Abstract

A mathematical model of a completely mixed activated sludge reactor was developed using Monod kinetics. The numerical solution of the resulting set of nonlinear differential equations was compared with the linearized analytical solution. The error between the nonlinear and linearized responses about an arbitrary steady state are shown for several step changes in inlet flow rate, carbon concentration, and sludge concentration. A stability analysis indicates that the reactor is stable over a wide range of operating conditions.

Response and Stability of a Completely Mixed Activated Sludge Reactor

The dynamics and control of chemical reactors have been studied widely in recent years (1, 2). If the dynamic characteristics of a chemical process are understood, a control scheme can usually be devised that will increase the quality of the product and reduce the operating costs. In the waste treatment field, there is a need to improve the performance of the activated sludge process. Although the principles used in analyzing the dynamics of biochemical and chemical reactions are similar, the dynamics and control of activated sludge reactors have not received much attention to date.

Eckhoff and Jenkins (3) proposed a mathematical model to describe the unsteady state behavior of a completely mixed activated sludge system. The results predicted by their mathematical model gave fair agreement with experimental data from a laboratory reactor subjected to a step change in the inlet substrate concentration. Knopp (4) developed linear approximating differential equations for a well mixed activated sludge reactor. He randomly varied the input substrate concentration to a laboratory reactor and measured the output responses. His model, however, did not adequately reflect the changes in effluent COD.

A control system for a reactor is usually designed to maintain some steady state condition while the process is subjected to a series of disturbances. The stability of the control system about the steady state can be analyzed by linear control theory, in which any nonlinear terms are approximated by a series expansion about the steady state. However, the stability of non-linear systems predicted by linear analysis is only valid for some region about the steady state.

The equations describing an activated sludge reactor contains non-linear terms. This paper will examine the non-linear and linearized responses of a well mixed activated sludge reactor to step changes in feed flow rate, carbon concentration, and sludge concentration. Since sewage treatment plants are usually subjected to changes of large magnitude, a wide range of input disturbances will be considered. The error between the linear and non-linear responses will be determined and compared. In addition, the results of the linear analysis will be used to examine the conditions over which the reactor will operate stably.

Model of Activated Sludge Reactor

Based on Monod type reaction kinetics for the disappearance of dissolved carbon and the generation of sludge, material balances can be made on the dissolved carbon and sludge flowing through the reactor. The reacting system is assumed to be agitated sufficiently so that the contents are completely mixed at any instant in time. A schematic representation of the reactor is shown in Figure 1.

A carbon balance around the reactor gives:

$$v_o C_o - vC - \left(\frac{k\,C\,C_M}{K + C}\right) V = V\frac{dC}{dt} \qquad (1)$$

Similarly, a material balance on the sludge is:

$$v_o\,C_{Mo} - vC_M + Y\,V\left(\frac{k\,C\,C_M}{K + C}\right) = V\,\frac{dC_M}{dt} \qquad (2)$$

where

C = carbon concentration

C_M = sludge concentration

v = volumetric flow rate

V = reactor volume

These simultaneous differential equations are nonlinear and must be solved numerically.

Linearized Equations and Solutions

Since a major use of a dynamic model will be in designing a control scheme and in system optimization, the reactor model will also be approximated by its linearized form. Linearization of the equations is accomplished by replacing the nonlinear terms by the appropriate multivariable Taylor series expansion, truncated after the first order term. We will consider step changes in the feed variables C_o, C_{No}, and v_o.

A. Step Change in Carbon Feed

The feed carbon concentration for a step input is $C_o\ (a + 1)$, where C_o is the initial steady state concentration and a is the magnitude of the step change. Linearizing the reaction rate expression around the steady state gives:

$$\text{Rate} = \frac{k\ C\ C_N}{K + C} = \frac{kC_s\ C_{Ns}}{K + C_s} + \frac{kK\ C_{Ns}}{(K + C_s)^2}\ (C - C_s) + \frac{k\ C_s}{K + C_s}\,(C_N - C_{Ns}) \qquad (3)$$

By substituting the linearized kinetics into equations (1)and (2), we obtain:

$$\frac{dC}{dt} = \frac{v_o}{V}\ C_o\ (a + 1) - \frac{v_o}{V}\ C - [\gamma + \beta\ (C - C_s) + \alpha\ (C_N - C_{Ns})\ ] \qquad (4)$$

$$\frac{dC_N}{dt} = \frac{v_o}{V}\ C_{No} - \frac{v_o}{V}\ C_N + Y\ [\gamma + \beta\ (C - C_s) + \alpha\ (C_N - C_{Ns})\ ] \qquad (5)$$

where

$$\alpha = \frac{k\ C_s}{K + C_s}$$

$$\beta = \frac{k\ K\ C_{Ns}}{(K + C_s)^2}$$

$$\gamma = \frac{k\ C_s\ C_{Ns}}{K + C_s}$$

Equations (4) and (5) are linear first order differential equations which can be solved analytically. For a given reactor and initial steady state condition, the terms α , β , γ , C_{Ns}, C_s, Y, C_o, C_{No}, V and v_o are constant. The solutions of equations (4) and (5) may be written as:

$$\frac{C}{C_s} = He^{\lambda_1 \theta} + Je^{\lambda_2 \theta} + \overline{C}_P \qquad (6)$$

$$\frac{C_M}{C_s} = Le^{\lambda_1 \theta} + Me^{\lambda_2 \theta} + \overline{C}_{MP} \qquad (7)$$

where

$$\theta = \frac{t\ v_o}{V} = \frac{t}{\tau}$$

$$\lambda_1 = -1 - \beta\tau + \alpha Y \tau$$

$$\lambda_2 = -1$$

$$\overline{C}_P = \frac{(1 - \alpha Y\tau)[(a + 1)(\frac{C_o}{C_s} + \delta)] + \alpha\tau(Y\delta - \frac{C_{Mo}}{C_s})}{(1 + \beta\tau)(1 - \alpha\tau Y) + (\alpha \beta Y \tau^2)}$$

$$\overline{C}_{MP} = \frac{(1 + \beta\tau)\frac{C_{Mo}}{C_s} - Y\delta + Y\beta\tau(a + 1)(\frac{C_o}{C_s})}{(1 + \beta\tau)(1 - \alpha\tau Y) + (\alpha \beta Y \tau^2)}$$

$$H = \frac{(1 - \overline{C}_P)(\frac{\beta}{\alpha}) - \frac{C_{Ms}}{C_s} + \overline{C}_{MP}}{\frac{\alpha Y - \beta}{\alpha}}$$

$$J = 1 - H - \overline{C}_P$$

$$L = -YH$$

$$M = -\frac{\beta}{\alpha} J$$

$$\delta = (\frac{\alpha C_{Ms}}{C_s} + \beta - \frac{Y}{C_s})$$

For a given set of conditions and step size, the concentration of carbon and sludge leaving the reactor can be found as a function of time.

B. Step Change in Sludge Concentration

The concentration of sludge entering the reactor is changed by the step function, C_{Mo} (a + 1). The linearized rate expression is substituted in equations (1) and (2) to describe the response of carbon and sludge concentrations to this step change.

$$\frac{dC}{dt} = \frac{v_o}{V} C_o - \frac{v_o}{V} C - [\gamma + \beta (C - C_s) + \alpha (C_M - C_{Ms})] \qquad (8)$$

$$\frac{dC_M}{dt} = \frac{v_o}{V} C_{Mo} (a + 1) - \frac{v_o}{V} C_M + Y [\gamma + \beta (C - C_s) + \alpha (C_M - C_{Ms})] \qquad (9)$$

The analytical solutions are the same as equations (6) and (7) except for the form of the particular solutions.

$$\bar{C}_P = \frac{(1 - \alpha Y \tau) (\frac{C_o}{C_s} + \delta) + \alpha \tau [(a + 1) (Y \delta - \frac{C_{Mo}}{C_s})]}{(1 + \beta \tau) (1 - \alpha \tau Y) + (\alpha \beta Y \tau^2)}$$

$$\bar{C}_{MP} = \frac{(1 + \beta \tau) (a + 1) \frac{C_{Mo}}{C_s} - Y\delta + Y\beta\tau (\frac{C_o}{C_s})}{(1 + \beta \tau) (1 - \alpha \tau Y) + (\alpha \beta Y \tau^2)}$$

C. Step Change in Feed Rate

In this case, the volumetric flow rate to the reactor is changed by the step function, v_o (a + 1). The linearized flow rate and kinetic terms are inserted in equations (1) and (2) to give:

$$\frac{dC}{dt} = \frac{[(C_o - C_s) v_o (a + 1) + v_o (C_s - C)]}{V} - [\gamma - \beta (C - C_s) + \alpha (C_M - C_{Ms})] \qquad (10)$$

$$\frac{dC_M}{dt} = \frac{[(C_{Mo} - C_{Ms}) v_o (a + 1) + v_o C_s (C_{Ms} - C_M)]}{V} + Y [\gamma - \beta (C - C_s) + \alpha (C_M - C_{Ms})] \qquad (11)$$

Again the analytical solutions of these equations differ from equations (6) and (7) only in the particular solutions:

$$\overline{C}_{MP} = \frac{(C_{Mo} - C_{Ms})\frac{a}{C_s} + \frac{C_{Mo}}{C_s} + (\frac{C_o}{C_s} - 1)(a + 1)\frac{Y\beta\tau}{1 + \beta\tau}}{1 - \frac{Y\alpha\tau}{1 + \beta\tau}}$$

$$\overline{C}_P = \frac{(C_o - 1)(a + 1) + 1 + \beta\tau - \alpha\tau\,\overline{C}_{MP}}{1 + \beta\tau}$$

Comparison of Linear and Non-Linear Solutions

Since the non-linear differential equations of the model cannot readily be solved analytically, kinetic constants and feed conditions are assumed and the resulting computer solutions are compared with the corresponding solutions from the linearized equations. The kinetic constants were estimated from the following steady state data on a municipal treatment plant (5, 6):

C_{Mo} = 2450 mg/l $\quad$ τ = 3.0 hours
C_M = 2500 mg/l $\quad$ $v_o = 4 \times 10^3$ ft^3/hr
C_o = 100 mg/l $\quad$ $V = 12 \times 10^3$ ft^3
C = 25 mg/l $\quad$ Y = 0.673

By substituting these data into the steady state form of equations (1) and (2), the kinetic constants were found to be:

$$k = .02 \text{ hr}^{-1}$$

$$K = 25 \text{ mg/l}$$

Using the above parameters, the non-linear equations (1) and (2) were solved for the response of the reactor to various step forcing functions. The same constants were also used in equations (8) to (11) to yield a linearized response.

The non-linear and linearized responses are compared for step changes in the three input variables on Figures 2 through 7. Responses are illustrated as plots of C/C_s vs. time and C_M vs. time for step changes of ± 50% and +100%. When the inlet concentration of carbon is subjected to a step change, the linear model underestimates the system response for a positive step and overestimates for a negative step. The reverse behavior is observed for a step change in inlet sludge concentration. When a step transient in either direction is imposed on the flow rate, the linear model overestimates the change in concentration. In general, the effluent carbon or sludge concentration closely approaches the new steady state concentration in less than 10 hours after the step change.

The absolute magnitude of the error between the non-linear and linear response is plotted against step size in Figures 8 to 10. The error is calculated from the final steady state concentrations as | Nonlinear - Linear | / | Nonlinear |. These figures show that the error is less than 10% for step changes up to ±30%. In the case of sludge concentration, the error between non-linear and linear responses is below 10% for step changes up to 100%.

Stability Analysis

For an unstable process in a linear system, the dependent variables usually approach infinity or saturation with increasing time. Non-linear systems, however, may have an unstable point where an arbitrarily small perturbation will cause the system to come to rest at a new point which is not necessarily infinity. Liapunov's first method can be applied to non-linear systems to determine which points are unstable. This theorem states that a sufficient condition for the origin of a non-linear system to be asymptotically stable is that the characteristic roots of the linearized system have negative real parts. If there is a characteristic root with positive real parts, the origin is unstable.

Applying Liapunov's theorem to equations (4) and (5), we find that the characteristic roots for the system of non-linear equations (1) and (2) are:

$$\lambda_1 = -1 - \tau(\beta - \alpha Y) \qquad (12)$$

$$\lambda_2 = -1 \qquad (13)$$

The roots do not depend on the nature of the input perturbation. Since the origin of the system of equations is C_s and C_{Ms}, the stability of the steady state concentration is being examined. By substituting for α and β in equation (12), we obtain

$$\lambda_1 = C_s^2(Yk - \frac{1}{\tau}) + C_sK\ (Yk - \frac{2}{\tau}) - K\ k\ C_{Ms} - \frac{K^2}{\tau}$$

For stability, $\lambda_1 \leq 0$. Therefore,

$$C_s^2\ (Yk - \frac{1}{\tau}) + C_sK\ (Yk - \frac{2}{\tau}) - Kk\ C_{Ms} \leq \frac{K^2}{\tau} \qquad (14)$$

Since C_s, C_{Ms}, k, and K, are $\geq$ 0, stability is assured if

$$Yk - \frac{1}{\tau} \leq 0 \qquad (15)$$

Since equation (15) is satisfied for almost all practical situations, the stable regions of operation are very broad. If the inlet reactor sludge concentration is zero, equation (14) will converge to the results found by Aris et al. (7). If equation (15) is not satisfied, the system still may be stable. By substituting values of the parameters into equation (14) stability can be determined for any particular case. In addition, the terms in equation (14) must satisfy the material balance equations (1) and (2) at steady state. Therefore, equations (1), (2), and (14) must be solved simultaneously to determine stability for the case of $Yk - 1/\tau > 0$.

Conclusions

The results of this study show linearized and non-linear responses agree within 10% for input step disturbances up to ±30%. Thus, linear systems analysis can be applied to design controllers that should operate satisfactorily over a practical range of input fluctuations. The use of a linear process model simplifies the design of a control system. An analysis of reactor stability indicates that the region of stable operation is very broad.

Acknowledgment

The authors appreciate the use of the IBM 360-65 system at the University of Connecticut Computation Center. This work was supported in part by F.W.P.C.A. Grant No. WPD 175-01-67.

Notation

a = step size of perturbation, fraction of steady state value

C = concentration of carbon, mg/l

C_M = concentration of sludge, mg/l

k = Monod reaction rate constant

K = Monod reaction rate constant

t = time from step perturbation, hr

v = volumetric flow rate, ft^3/hr

V = volume of reactor, ft^3

Y = sludge produced/carbon consumed, mg/mg

θ = dimensionless time, t/τ

τ = steady state residence time, hrs

Subscripts:

o = inlet conditions

s = steady state conditions before step change

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Figure Titles

Figure 1. Schematic diagram of a completely mixed activated sludge reactor.

Figure 2. Exit carbon response to step changes in inlet carbon concentration.

Figure 3. Exit sludge response to step changes in inlet carbon concentration.

Figure 4. Exit carbon response to step changes in inlet sludge concentration.

Figure 5. Exit sludge response to step changes in inlet sludge concentration.

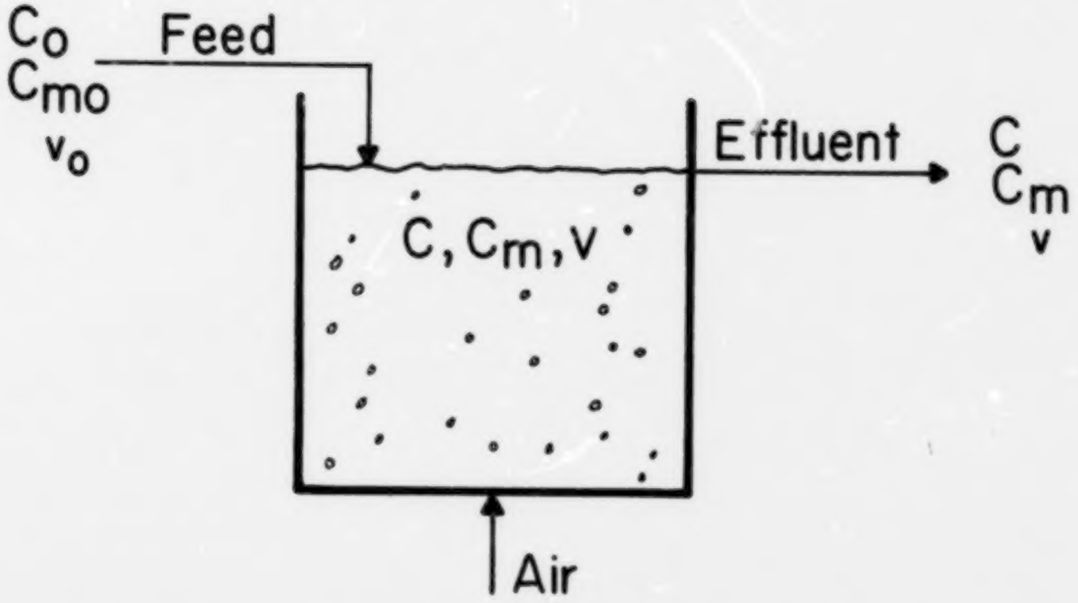
Figure 6. Exit carbon response to step changes in inlet feed rate.

Figure 7. Exit sludge response to step changes in inlet feed rate.

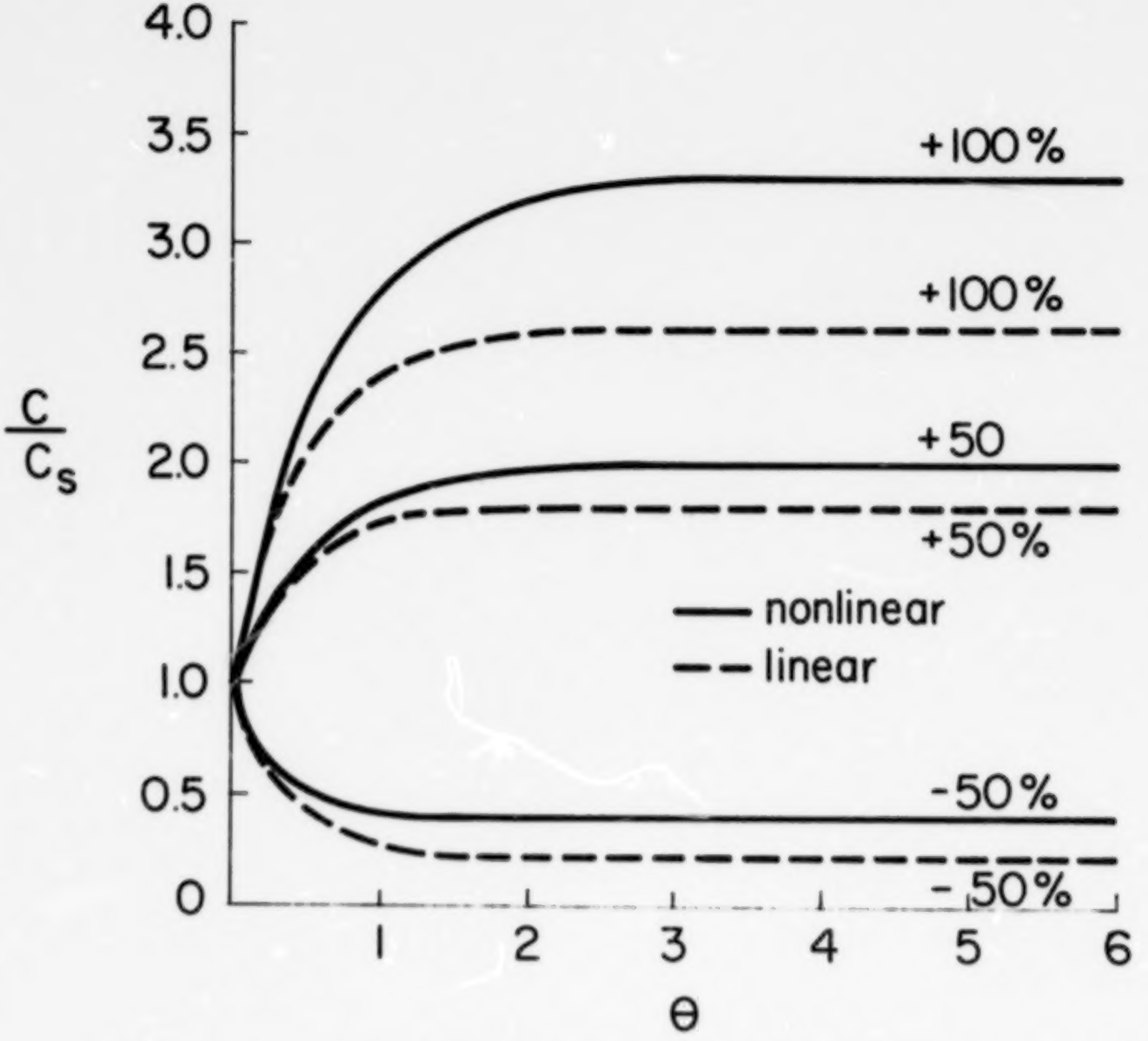
Figure 8. Error between nonlinear and linear steady state concentrations after step changes in inlet carbon concentration.

Figure 9. Error between nonlinear and linear steady state concentrations after step changes in inlet sludge concentration.

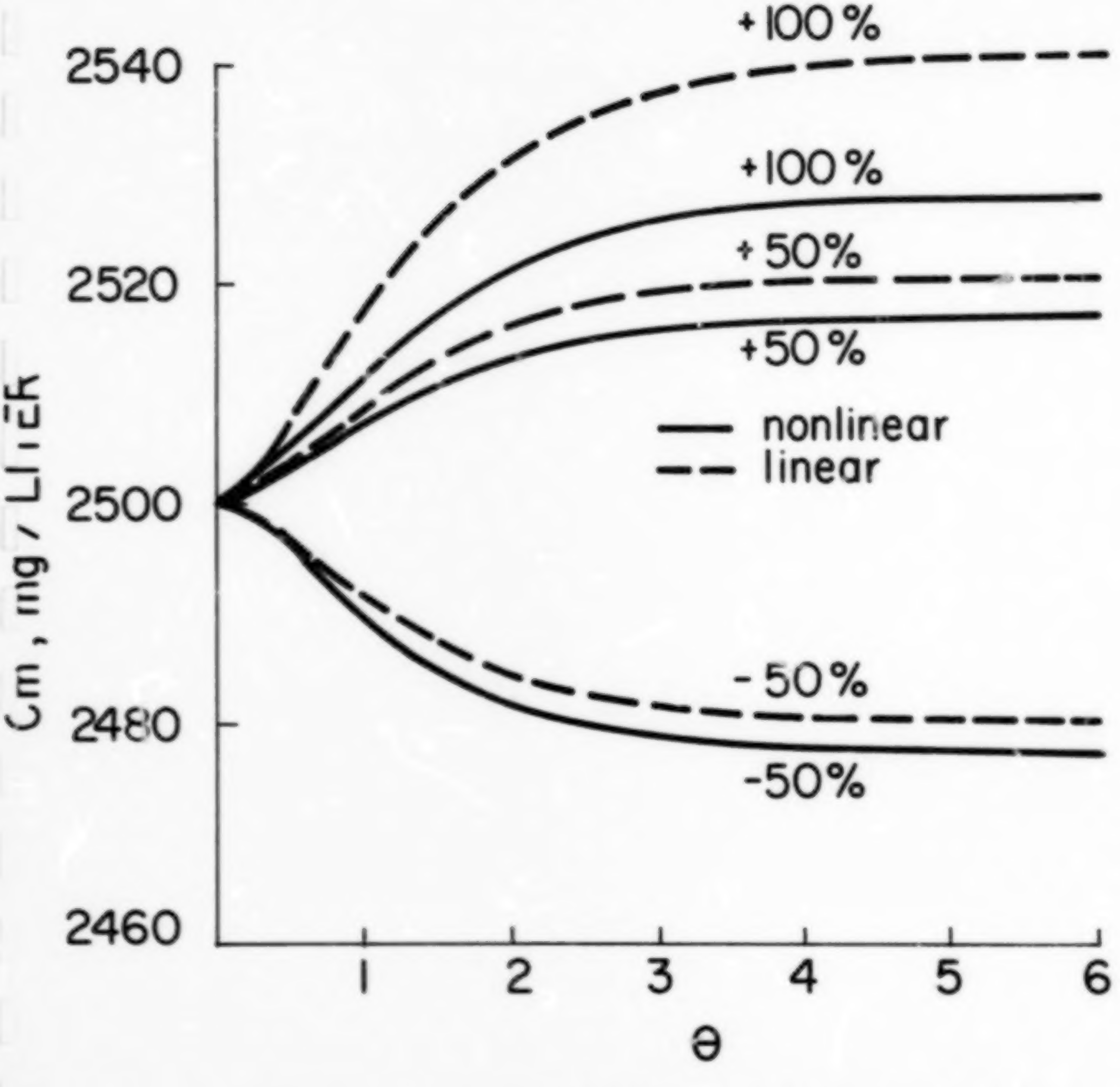
Figure 10. Error between nonlinear and linear steady state concentrations after step changes in inlet feed rate.


C_o
C_{mo}
v_o
Feed
Effluent
C
C_m
v
C, C_m, v
Air

SCHEMATIC DIAGRAM OF A COMPLETELY MIXED ACTIVATED SLUDGE REACTOR.



EXIT CARBON RESPONSE TO STEP CHANGES IN INLET CARBON CONCENTRATION.



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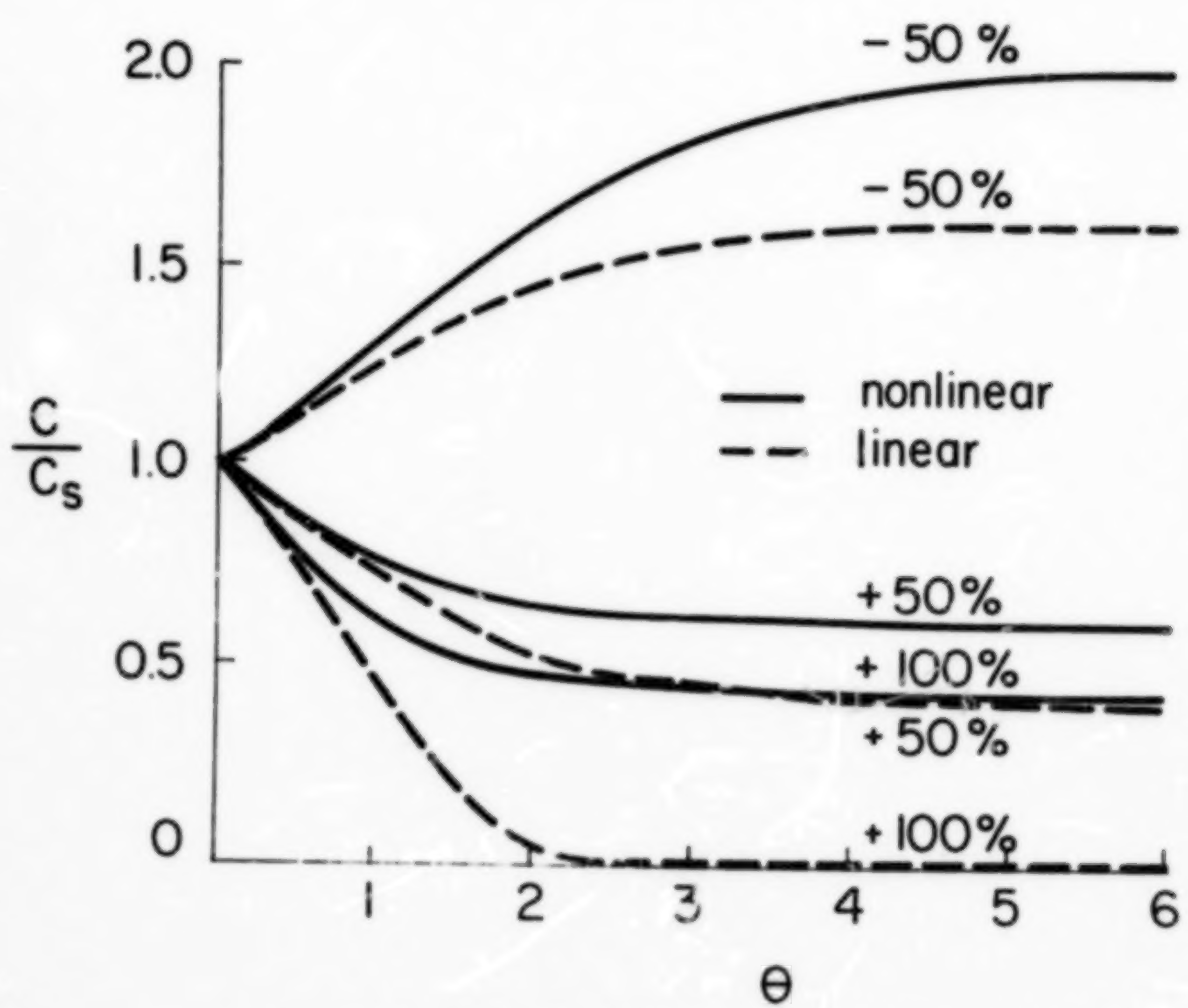

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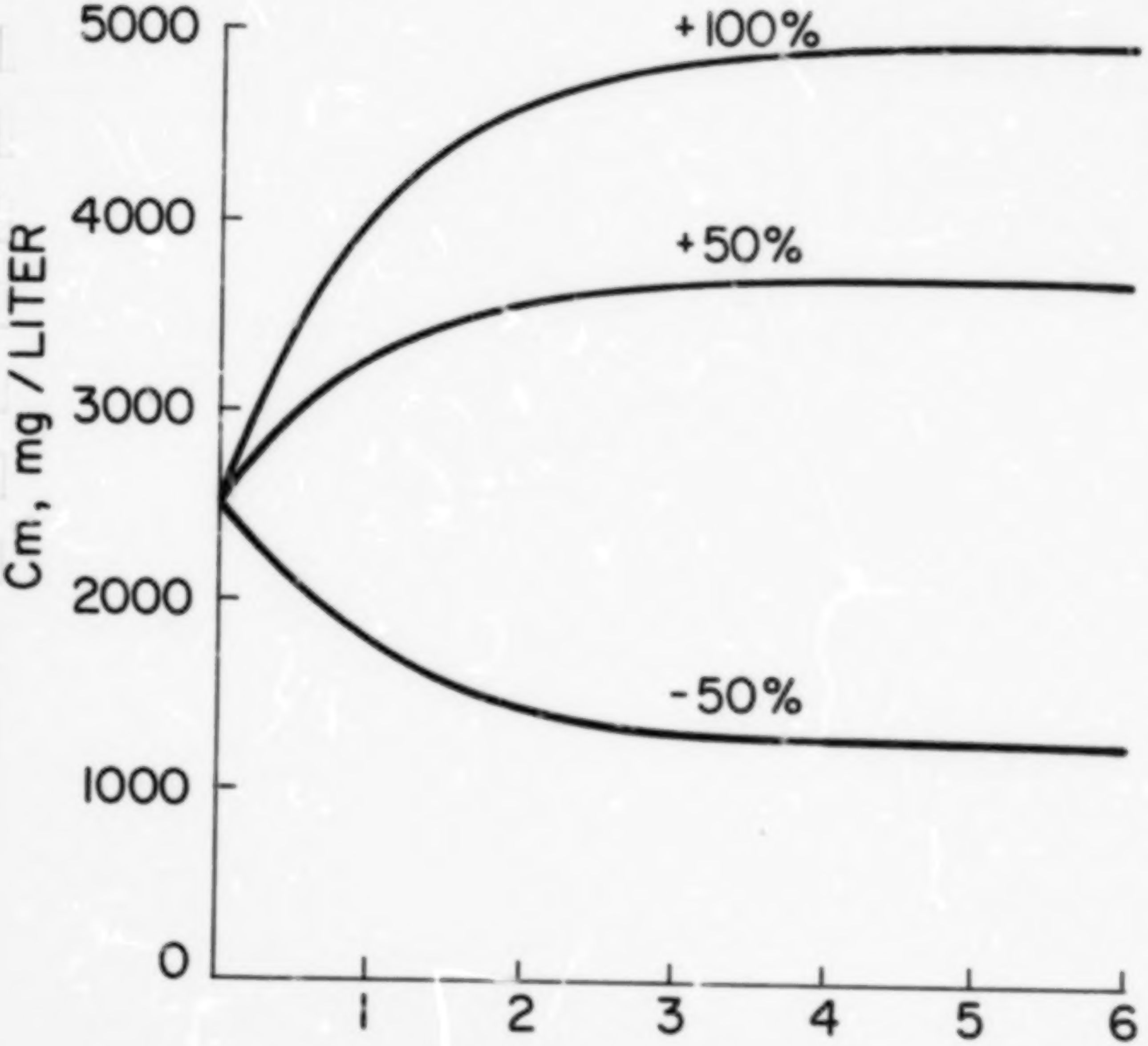
IN INLET SLUDGE CONCENTRATION.



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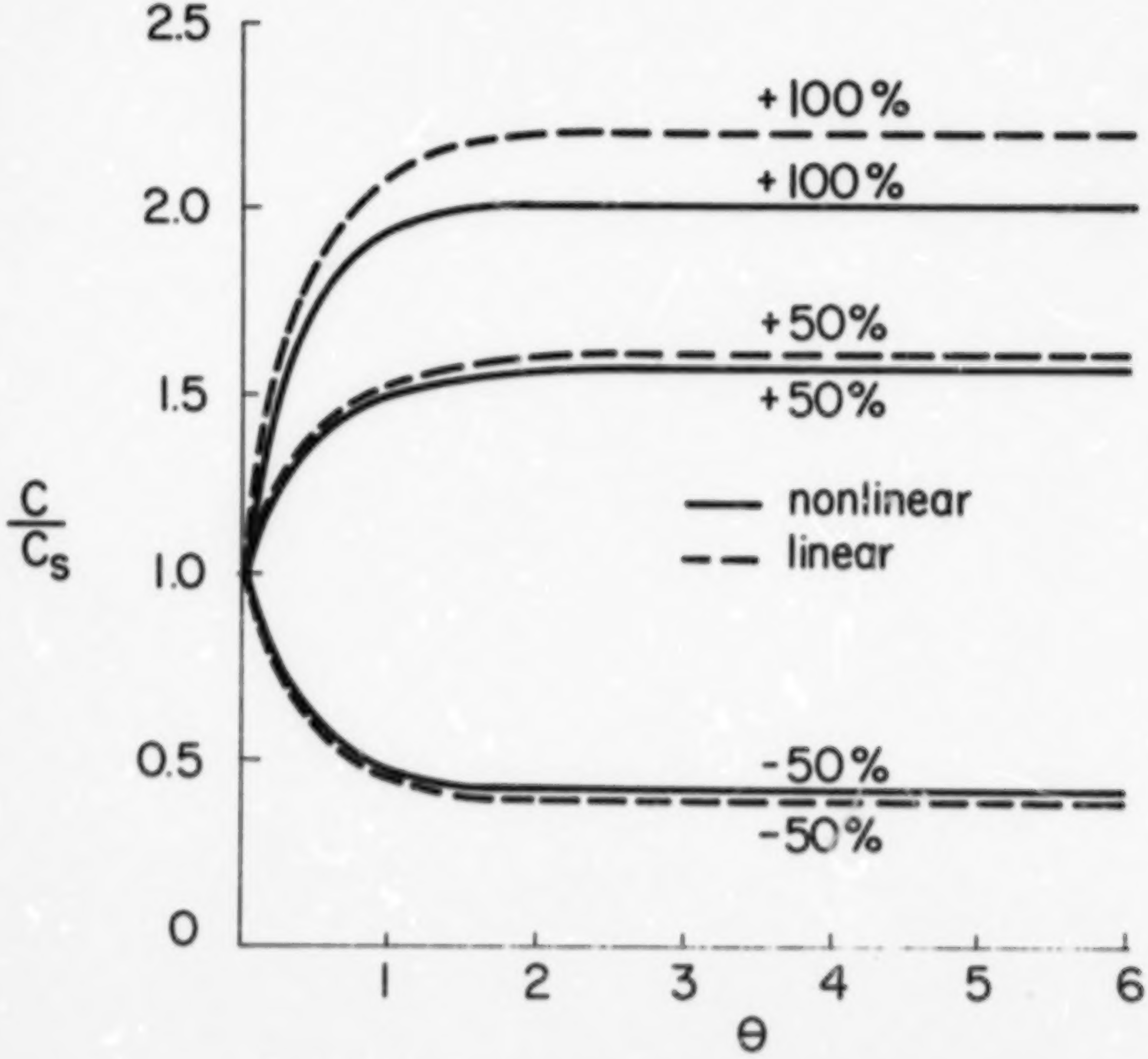
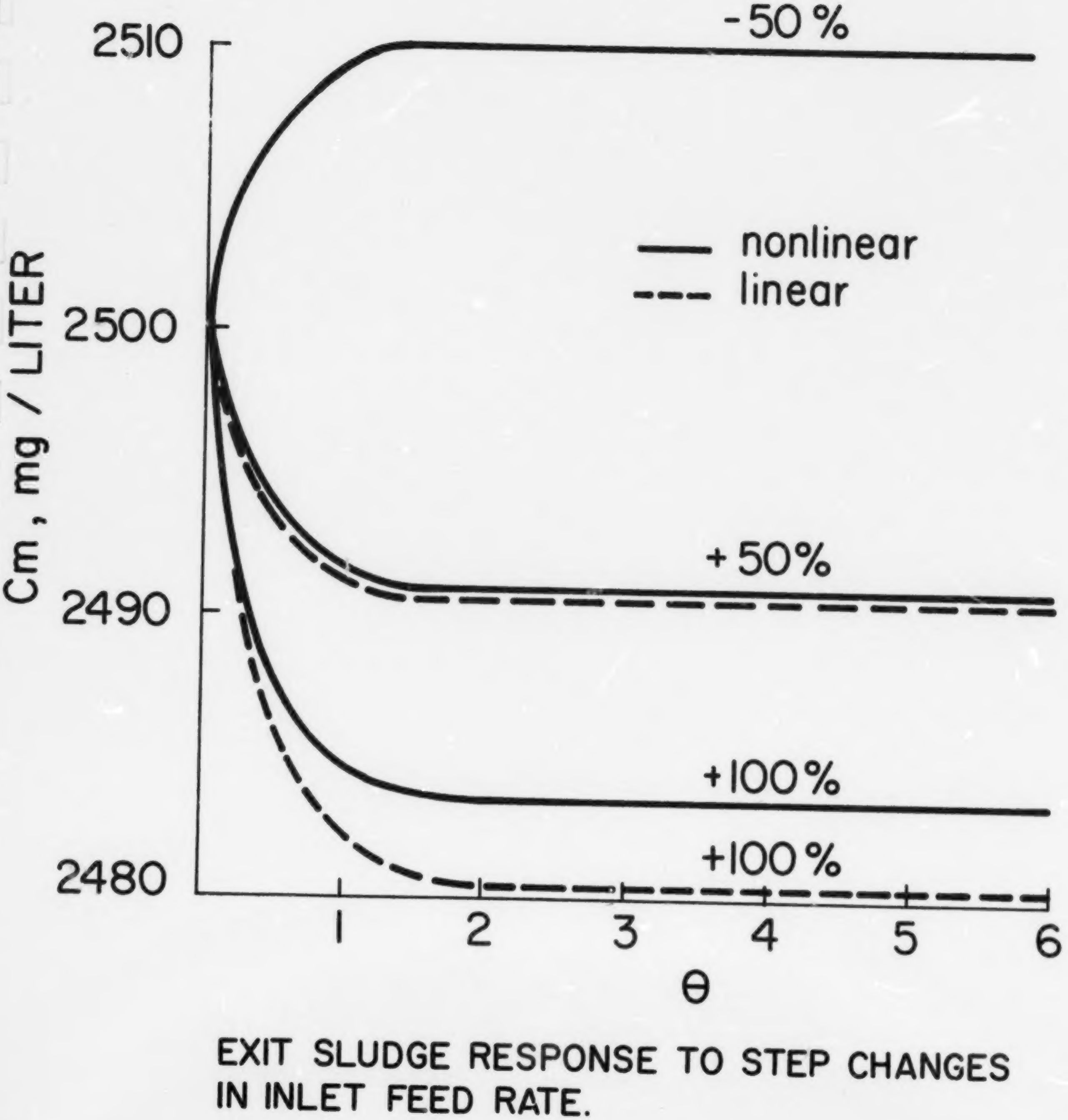


EXIT CARBON RESPONSE TO STEP CHANGES IN INLET FEED RATE.



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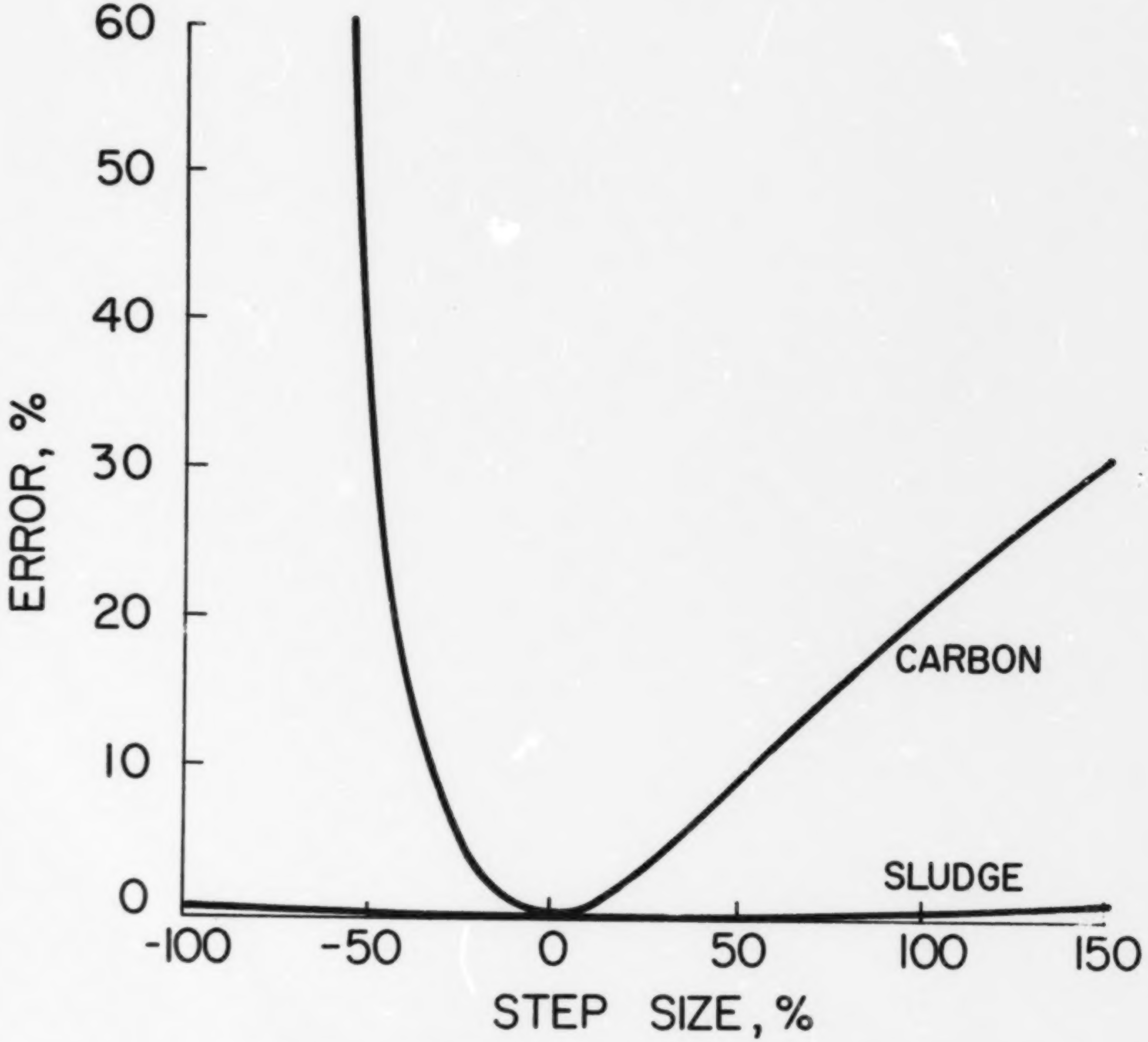
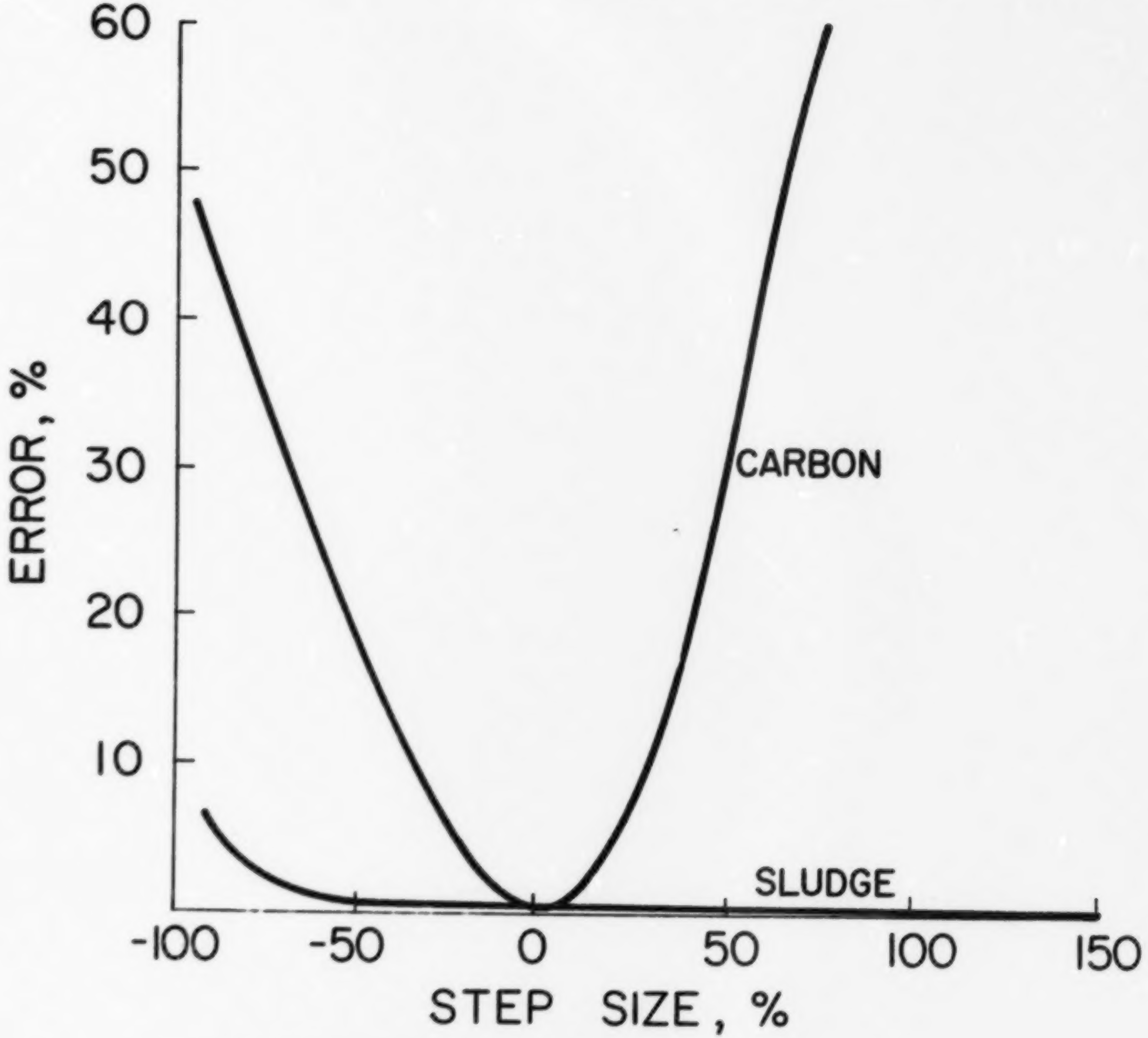


ERROR BETWEEN NONLINEAR AND LINEAR
STEADY STATE CONCENTRATIONS AFTER STEP
CHANGES IN INLET CARBON CONCENTRATION.



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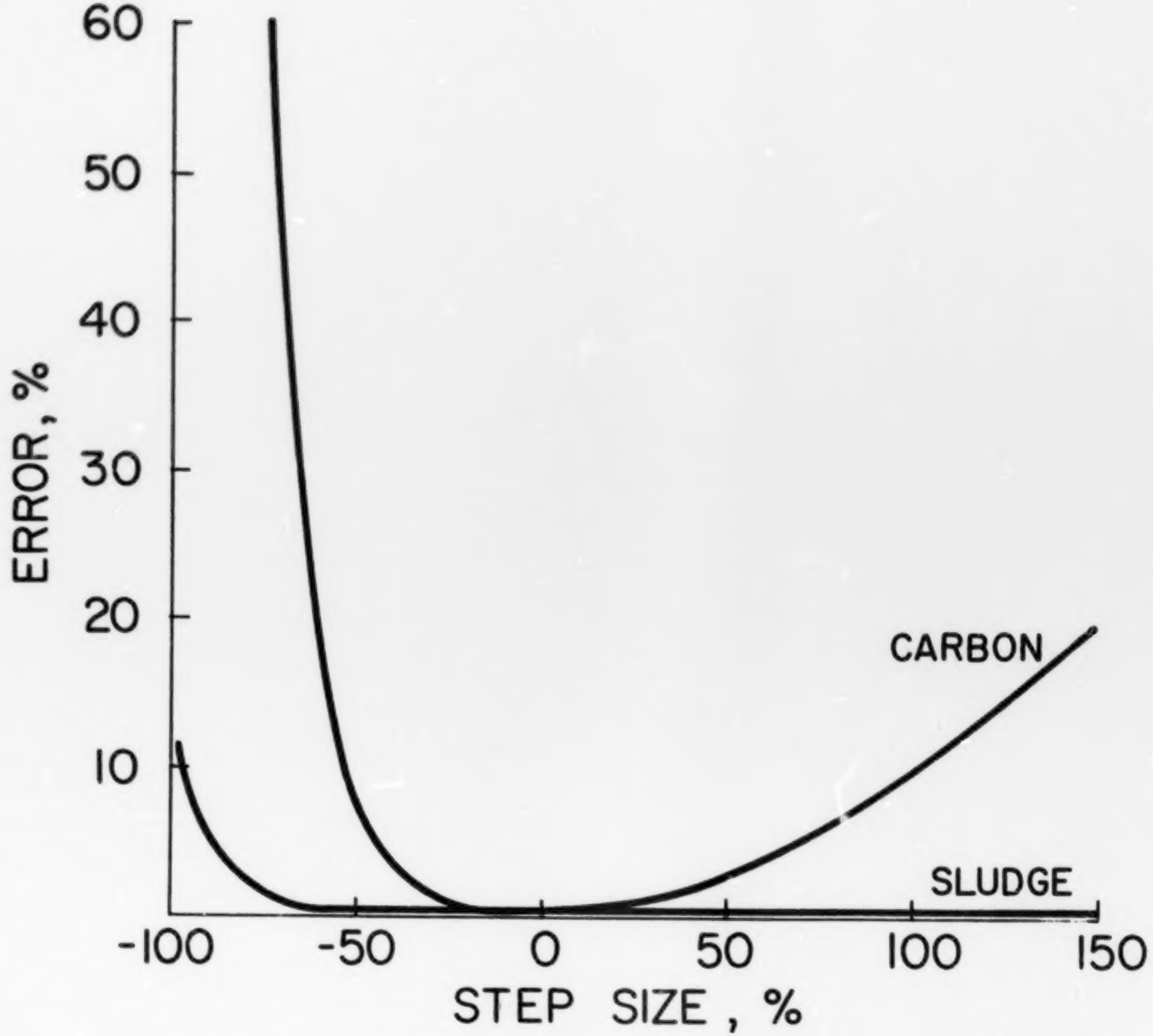

ERROR BETWEEN NONLINEAR AND LINEAR STEADY STATE CONCENTRATIONS AFTER STEP CHANGES IN INLET FEED RATE.